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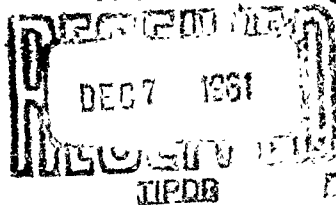
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AUTOCLAVE TESTING OF
MONEL, NICKEL AND INCONEL

MND-E-2655

October 1961

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FOREWORD

This report is submitted by the Nuclear Division of the Martin Company to the Nuclear Power Field Office, Engineer Research and Development Laboratories, US Army Corps of Engineers. The report was prepared under Contract DA-44-009-ENG-3581 and describes autoclave tests on Monel, nickel and Inconel coupons.

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SUMMARY

Stressed and unstressed specimens of Monel, nickel and Inconel were exposed to varied environmental conditions to test the resistance of these three metals to corrosion. The experiments were conducted in autoclaves operated at 450°F and 422 psia for 50, 200 and 2000 hours. The environmental conditions included variations in concentration of chloride, oxygen, phase (liquid or vapor) and method of pH adjustment. Statistical methods were employed in designing the experiments and in analyzing the results.

An incipient surface dulling was noted on some of the specimens that were tested for 50 and 200 hours, but none of the specimens cracked or pitted. No cracking of any coupons was observed in the 2000-hour autoclave tests, but varying degrees of pitting did occur for all three metals.

Typical corrosion rates from the 2000-hour data for coupons exposed to 1000 ppm chloride and 15 ppm oxygen were: Monel, 0.50 mdd; nickel, 0.38 mdd; and Inconel, 0.02 mdd.

Based on the results of these tests, the materials are listed in order of preference as follows: Inconel, nickel and Monel.

I. INTRODUCTION

The susceptibility to stress corrosion cracking of the austenitic stainless steels has resulted in concern over the use of these materials in nuclear power plant components, particularly the steam generator, of pressurized water plants. The danger of cracking can be avoided by using a material not subject to stress corrosion cracking or by deionizing and degassing the water to remove all dissolved materials. In many cases, it is economically impractical to treat the secondary water in this way. Furthermore, for military plants at remote sites (which are of primary concern in the ANPP Corrosion Program), it is highly desirable to reduce or, if possible, entirely eliminate the need for secondary water treatment. Hence, the use of a material immune to stress corrosion cracking is indicated. Of course, good resistance to general corrosion is also an essential requirement of potential materials. This report describes autoclave tests of several materials which hold promise of satisfying these corrosion requirements.

It is known that resistance to cracking increases with nickel content of the metal and that large additions of nickel are required for substantial improvement. Figure 1, which is reproduced from Ref. 26, indicates that approximately 50% nickel is required to ensure substantial immunity to cracking. Somewhat lower values have been reported by other investigators; nevertheless, it appears that at least 35 to 40% nickel is required.

Three nickel alloys have been investigated in this program: Monel, composed of 65% nickel, 33% copper, 1% iron; nickel "A", 99% nickel; and Inconel, composed of 77.3% nickel, 15.3% chromium and 6.2% iron. Stressed and unstressed specimens were tested in rocking autoclaves. Severe environmental variations of oxygen and chloride concentration were deliberately used to test the resistance of the materials to general and stress corrosion. Additional information on Monel, Inconel and nickel is being obtained from recently completed tests with miniature heat exchangers and somewhat larger model heat exchangers.
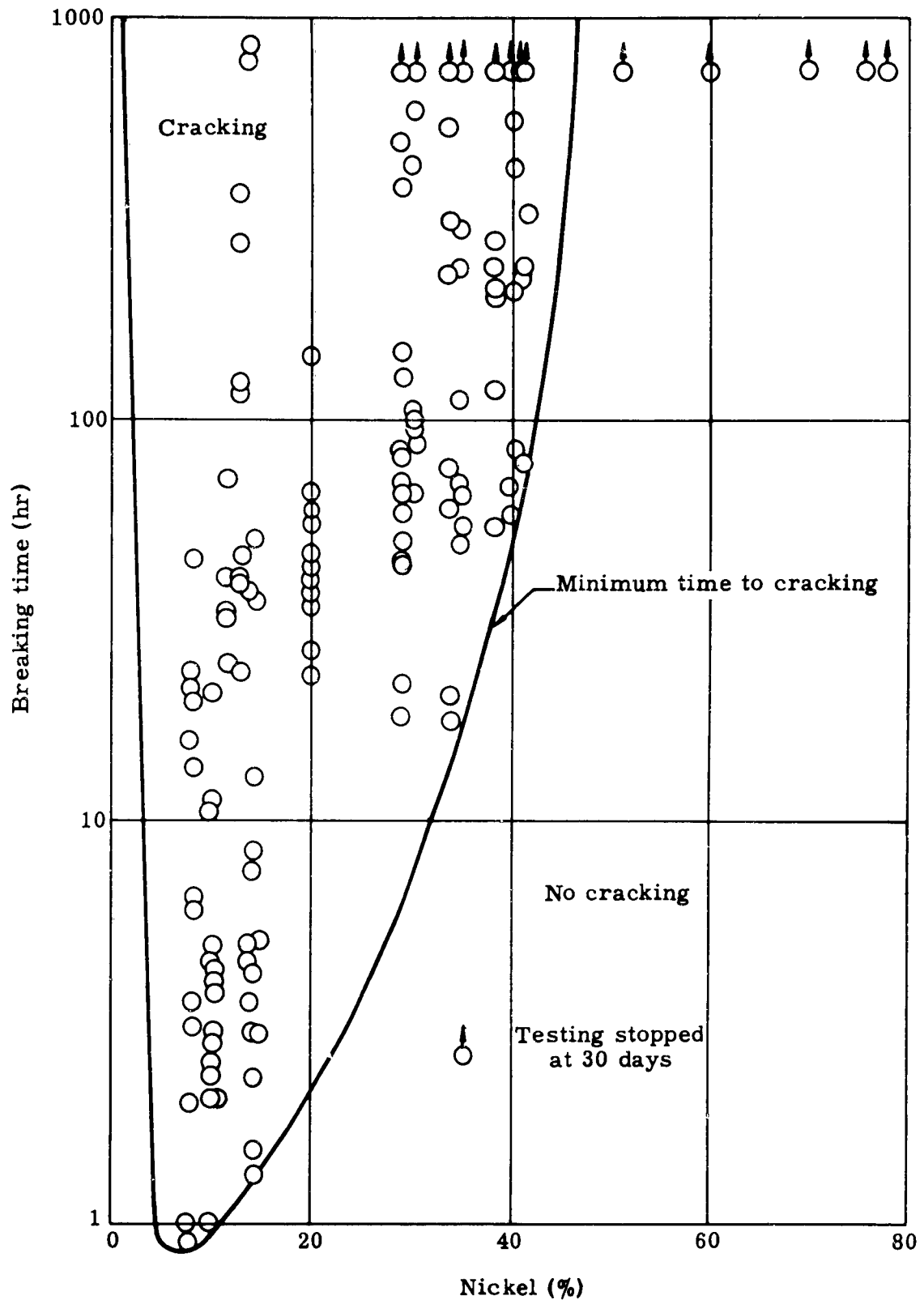
Fig. 1. Breaking Time of Iron-Nickel-Chromium Wires in Boiling
42% Magnesium Chloride (Ref. 26)

II. LITERATURE SURVEY

A literature survey on the corrosion resistance of Monel and nickel in high temperature water systems was conducted to supplement the autoclave test data. As expected, few references were found that were directly concerned with the subject. The reason for this is that Monel and nickel are not normally used in this application, generally for reasons of economy. However, the stringent demands for safety and long life in nuclear plant designs have considerably broadened the list of metals and alloys potentially applicable to these systems. Thus, Inconel, which has already received considerable attention in recent years, Monel and nickel must be considered in attempting to find the best materials for the fabrication of nuclear power plant components.

The bulk of available information on Monel and nickel is concerned with their use in the chemical processing industry--a use for which they are very well suited. It has been established that nickel possesses a high degree of resistance to corrosion by distilled and natural waters (Ref. 1). Solutions of neutral and alkaline salts like chloride have little corrosive action on nickel and nickel alloys (Refs. 1 and 12). These materials also possess high resistance to mineral and organic acids and most gases, including high temperature steams. Monel is highly resistant to the corrosive action of both fresh and salt water and especially to the effects of impingement and cavitation in sea water under conditions of high velocity (Ref. 12). In stagnant sea water, accumulations of marine organisms may result in pitting of the metal under the organisms.

It has been shown that Monel, nickel and Inconel are not subject to season cracking when used under stress conditions, while stress corrosion cracking has been observed only when they are in contact with a few selected chemicals, such as fused caustic soda and salts of mercury. In concentrations of caustic soda under 75 weight percent no caustic embrittlement of nickel, Monel and Inconel has been found, and if the metal is annealed prior to exposure, embrittlement by fused caustic can be avoided.

A corrosion test program which included these materials was undertaken at KAPL and then, at a later date, at Battelle Memorial Institute (Ref. 2). It was shown from this test program that the main advantage of Inconel is its resistance to chloride stress corrosion cracking, especially where there is the possibility of exposure to saline environment. Also, it indicated that Inconel can be classified as an acceptable construction material for primary water systems of pressurized water reactors.

Nuclear power plant steam generator tubing materials were tested for their susceptibility to chloride stress corrosion cracking (Refs. 3 and 4). Stressed U-bend specimens were exposed for 24 hours, in

tilting autoclaves, to both the liquid and vapor phases of a high pH synthetic boiler water solution containing oxygen, phosphate and chloride ion. The results indicated that Inconel, Monel and nickel displayed complete corrosion resistance.

Experience has shown that the high nickel alloys, Monel and Inconel, are not susceptible to stress corrosion cracking and would be promising materials from which to fabricate reactor steam generators (Refs. 5 and 13).

Berry and Fink (Ref. 5) conducted a research study on the general corrosion behavior of Monel in primary water; also determined were the effects of a number of conditions which may be present in secondary boiler water on the corrosion resistance of Monel. Monel specimens that were exposed for 2000 hours in flowing, 550° F hydrogenated primary waters were covered with an adherent dark brown tarnish film. Metallographic examination of selected samples from static and dynamic loop tests revealed no intergranular attack.

An investigation (Ref. 6) was conducted at the Westinghouse-Bettis plant to find an alternate material for austenitic stainless steel which would be satisfactory for use in pressurized water reactor plant steam generators and would not be subject to chloride stress corrosion cracking. After a preliminary broad evaluation, the field of investigation was narrowed to certain selected materials. The results of the extensive testing on the selected materials showed Inconel, Monel and nickel to have resistance to chloride stress corrosion cracking sufficient to justify a more thorough study of their suitability for use in pressurized water reactor plant steam generators.

To qualify Inconel for service in steam generators in pressurized water nuclear power plants, its behavior was investigated with respect to fabrication and resistance to corrosion (Ref. 7). Corrosion tests were conducted in simulated primary and secondary reactor waters on Inconel specimens in several conditions of heat treatment and composition. Inconel does not suffer intergranular attack or stress corrosion cracking in reactor waters. Therefore, it is considered an excellent material for fabrication of components exposed to primary and secondary water in pressurized water reactor systems.

Experiments were conducted by Howells, McNary and White (Ref. 8) to determine the corrosion resistance of various tube alloys to boiler sludge under steaming conditions. These experiments consisted of operating the model vessels as steam generators for periods lasting from one month to a year at conditions simulating those which would prevail in full-scale units. The results of the test, with chloride ion and dissolved oxygen in the secondary water, showed that Inconel was the material most resistant to the test environment.

A program to evaluate the corrosion resistance of materials considered for use in high temperature water systems was undertaken at Argonne National Laboratory (Ref. 9). The materials studied included nickel and nickel alloys. These tests were carried out, for the most part, in autoclaves. Monel and Inconel showed good corrosion resistance in oxygenated water at 500° F for periods of from two weeks to four months.

In static deionized water containing hydrogen, Inconel does not corrode (Refs. 2 and 10). However, if sulfide is present in a reducing atmosphere, the resulting hydrogen sulfide selectively reacts with nickel to produce nickel sulfide, which forces the alloy grains apart, resulting in rapid failure. The rate of corrosion is slower in an oxidizing atmosphere because the formation of nickel oxide inhibits sulfur attack. Inconel corrodes at a slower rate in static, deoxygenated, deionized water, ammoniated deionized water and air-saturated deionized water. Significant amounts of corrosion products are formed. Erosion of these products by flow of secondary water would raise the crud level and also might increase the corrosion rate. Inconel is also subject to pitting in crevices where differential oxygen concentration cells can occur in oxygen-bearing water under dynamic conditions.

Tests were performed to determine the corrosion resistance of a number of metals in high purity water at 500° F (Refs. 4 and 11). The resistance to corrosion of the three metals was found to be intermediate for nickel, with Inconel and Monel showing higher resistance. Of the factors affecting corrosion, the system temperature, the system gas concentration (particularly with respect to dissolved oxygen) and the metal surface preparation were found to be most important.

Nickel and the high nickel alloys, such as Inconel and Monel, have very good resistance to corrosion in degassed water and particularly in hydrogenated water. One of the most significant properties of the high nickel alloys is their resistance to stress corrosion cracking in chloride environments (Refs. 10 and 13).

Dynamic tests of model steam generators and superheaters at The Martin Company (Ref. 14) have shown that Inconel is well suited for heat exchanger application. These units were tested for extended periods, without failure, under severe environmental conditions. Earlier autoclave work (Ref. 15) had shown that Inconel is not susceptible to chloride stress corrosion cracking.

A few general statements concerning the resistance of Monel, nickel and Inconel to various environments are appropriate. These are enumerated on the following page.

(1) Nickel, Inconel and Monel show practically complete resistance to corrosion by alkaline solutions. Although caustic embrittlement has been encountered in solutions exceeding 75% concentration, this can be avoided by annealing the material prior to exposure.

(2) Nickel, Inconel and Monel are resistant to chloride attack at temperatures much higher than required for nuclear power plant service.

(3) Monel, Inconel and nickel are unaffected by steam at temperatures much higher than required for nuclear power plant service.

(4) The resistance of Inconel, Monel and nickel to chloride stress corrosion is good; however, they are subject to pitting in high temperature oxygenated water.

(5) High localized stresses tend to increase the corrosion rate in an oxidizing atmosphere.

(6) The corrosion rates of nickel, Monel and Inconel in high temperature water are comparable to the austenitic stainless steels.

(7) Stress corrosion cracking has been observed only in contact with a few specific chemicals, such as salts of mercury and fused caustic soda.

III. TEST SPECIMENS

A. PRETEST ANALYSIS

The three test materials underwent thorough physical and chemical examination prior to testing. Samples of each of the three were analyzed spectroscopically. The compositions are given in Table 1. All compositions were within commercial limits.

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TABLE 1

Composition of Test Materials

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	Nickel "A" (%)	Monel (%)	Inconel (%)
Nickel	99.5	65.0	77.28
Copper	0.02	32.65	0.07
Chromium	--	--	15.28
Iron	0.07	1.11	6.22
Manganese	0.28	0.95	0.68
Silicon	0.04	0.16	0.20
Carbon	0.09	0.12	0.05
Phosphorous	--	--	0.01

A number of supplemental tests were performed on autoclave specimens and on the specimen materials to provide data to establish specimen parameters for the autoclave program. These included tensile tests on Monel, nickel and Inconel specimens, determination of strain-deflection curves for autoclave specimens and a determination of the mean surface area of the coupons.

Six Monel and six nickel tensile specimens were fabricated from the same material used for the autoclave coupons. The tensile specimens were machined after the final roll to 0.040-inch thickness; test specimens were cut from the same material (see Section B). One half of the Monel and nickel tensile specimens were fully annealed at 1450° F and 1350° F, respectively, for one hour, along with the respective test coupons. The other half of the tensile specimens were stress-relieved, along with the respective test coupons, at 450° F for one hour. The re-

sults of the tensile tests on these specimens, and Inconel specimens similarly prepared, are shown in Table 2. The values given are averages of three determinations. Deviations from the averages were less than 2% in all cases.

Figure 2 shows a typical stress-strain curve for stress-relieved Monel. A stress level of 90% of the yield strength (0.2% offset) was chosen arbitrarily for stressing the autoclave beam specimens. The total strain associated with 90% of yield stress was determined directly from the curve. For example, in Fig. 2, this total strain is 0.00433 in./in.

TABLE 2

Physical Properties of Autoclave Coupon Materials
(average of 3 values)

	Yield Strength (psi)	90% of Yield Strength (psi)	Proportional Limit (psi)	Ultimate Tensile Strength (psi)	Modulus of Elasticity (x 10^6)	Percent Elongation (2 in.)
Monel (stress-relieved)	123,700	111,000	79,000	126,470	28.0	28.0
Monel (annealed)	33,015	27,000	28,000	78,630	24.5	24.5
Nickel (stress-relieved)	109,060	98,200	82,000	121,665	32.0	32.0
Nickel (annealed)	19,115	17,200	10,250	74,080	29.1	29.1
Inconel (stress-relieved)	166,600	149,940	131,600	169,600	29.6	29.6
Inconel (annealed)	32,860	29,574	23,600	93,200	26.7	26.7

Strain-deflection curves were determined for several typical beam-type specimens. An SR-4 strain gage was attached at the center of the coupons, which were then deflected in 5-mil increments. Figure 3 shows the test rig with the depth gage used to measure deflection. (The strain gage had not been attached when the photo was taken.) Since the strain-deflection relationship is independent of material properties, the same
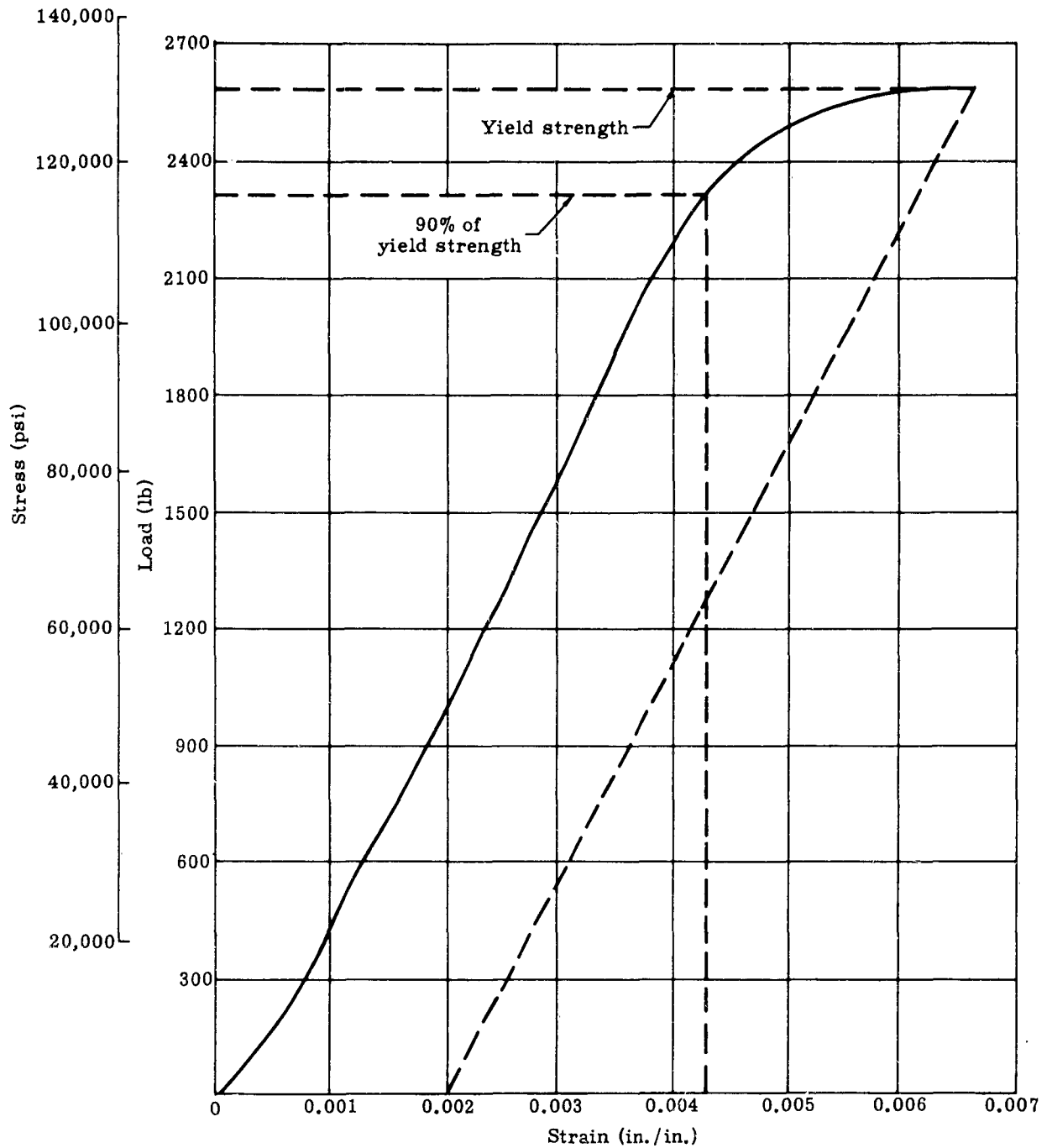
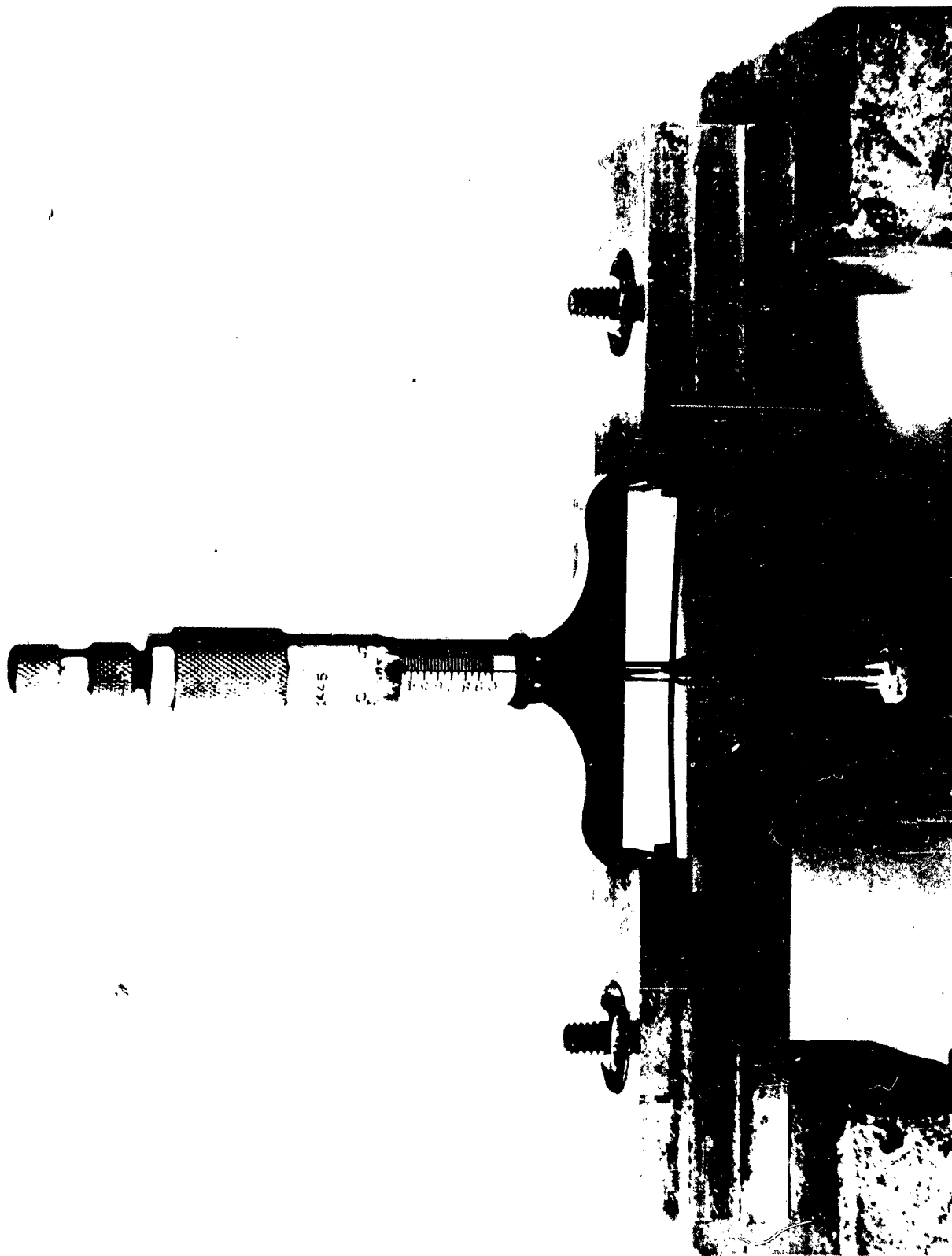Fig. 2. Stress-Strain Curve for Stress Relieved Monel

Fig. 3. Test Rig with Depth Gage Used to Measure Deflection

curve (Fig. 4) was used for all coupons. This was verified by testing several materials and heat treats. The deflection required to produce the strain corresponding to 90% of yield stress was determined from Fig. 4. This same deflection was established in the autoclave holder for the stressed coupons. The deflections employed are listed in Table 3.

TABLE 3

Summary of Required Coupon Deflections

Material	Condition	Deflection (mils)
Monel	Fully annealed	46.0
Monel	Stress-relieved	126.0
Nickel	Fully annealed	18.5
Nickel	Stress-relieved	86.0
Inconel	Fully annealed	42.0
Inconel	Stress-relieved	155.0

The surface area of the autoclave specimens is important in interpreting the corrosion data. However, because of the large number of specimens involved, individual measurement of surface area would be excessively time-consuming. In order to determine the deviation among specimens, micrometer measurements were made on 50 randomly selected coupons of each metal, and the surface areas were determined. The surface areas of all coupons checked fell within ±0.8% of the mean area. Additionally, measurements were made on the coupons used in the first autoclave run and the same close tolerances were observed. Therefore, the average area (3.3 square inches for each material) was used in the analysis of the results.

B. SPECIMEN PREPARATION

The material supplier selected specified amounts of Monel and nickel tubing, 2-1/2 inches in diameter with 5/16-inch wall thickness, from individual heats. Some of this tubing was drawn to 3/4-inch OD with a
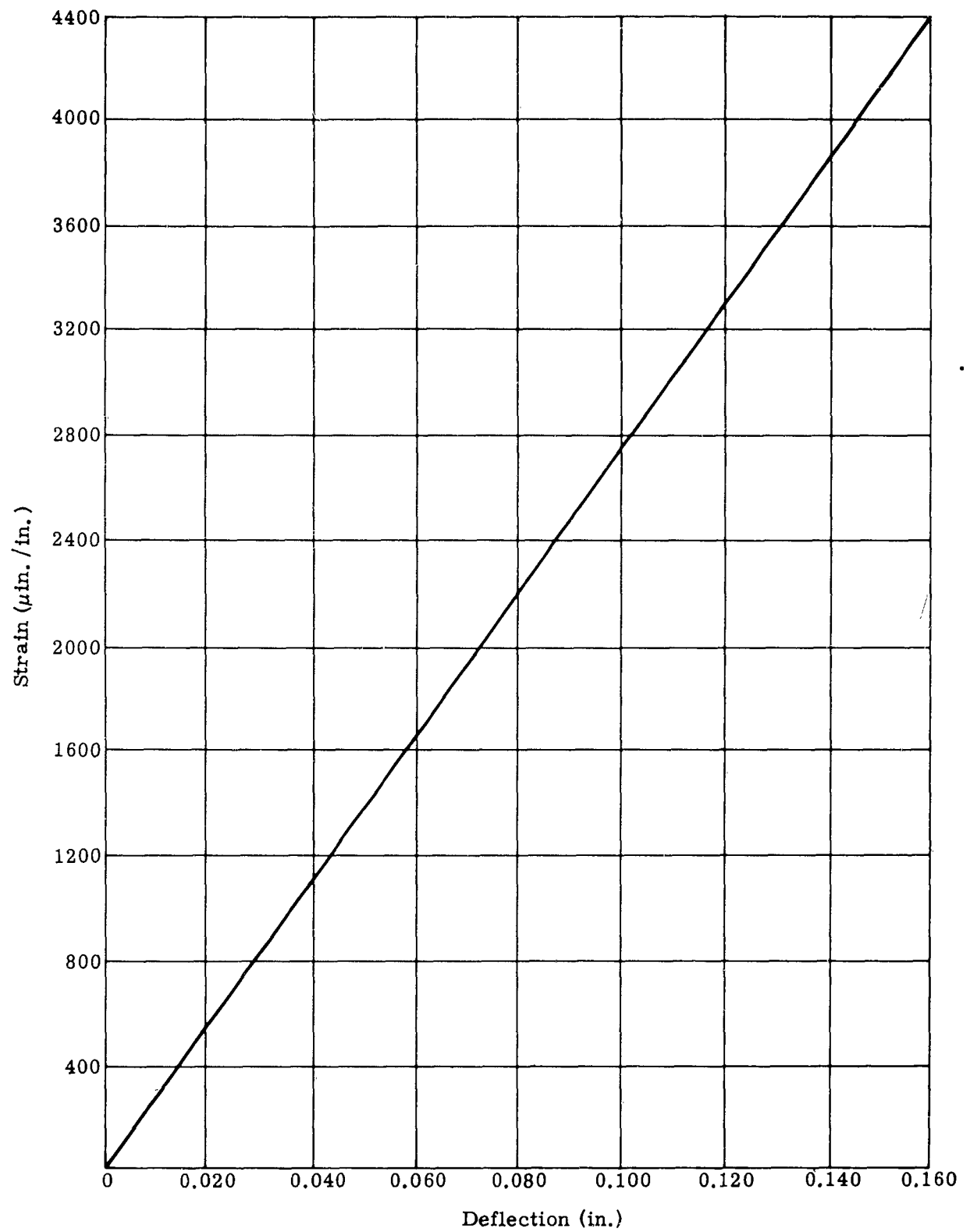
Fig. 4. Strain Versus Deflection Curve for Autoclave Coupon Materials

0.65-inch thick wall. This tubing was set aside for use in the fabrication of test heat exchangers. The remainder of the tubing was split, flattened and rolled to sheet, 3 inches wide, 1/8 inch thick and 72 inches long.

The as-received sheet was rolled to 0.080 inch and fully annealed: Monel was annealed in a hydrogen atmosphere at 1450° F for one hour; nickel was annealed in a hydrogen atmosphere at 1350° F for one hour. The annealed strips were deoxidized, then further reduced to 0.040-inch thickness, producing 50% coldwork. Test coupons and tensile specimens were sheared and numbered. The coupons were rinsed in acetone, pickled in dilute hydrochloric acid, rinsed in hot distilled water and dried in a heated air blast to prevent water staining. Half of each type of coupon was fully annealed, as above, and the remainder of both types of coupon was stress-relieved at 450° F for one hour.

The Inconel specimens were prepared in the same manner, i.e., 0.080-inch Inconel sheet was fully annealed at 1800° F for 15 minutes in a hydrogen atmosphere. The thickness was reduced to 0.040 inch, which produced 50% coldwork. Tensile specimens and test coupons were sheared, and half of each was annealed at 1800° F for 15 minutes in a hydrogen atmosphere and the other half was stress-relieved at 800° F in air for one hour.

All of the test coupons--Monel, Inconel and nickel--were 3 inches long, 1/2 inch wide and 0.040 inch thick.

C. SPECIMEN HOLDERS

The holders for the specimens were fabricated of Inconel with teflon and diamonite insulators. Each holder supports 12 specimens, six stressed and six unstressed. The beam specimens were supported at both ends. Stress was applied by adjusting a fine-thread screw, which loaded the beam at the midpoint. Two holders were used in each autoclave, one in the liquid phase and one in the vapor phase. Figure 9 is a photograph of the sample holder with coupons mounted.

IV. EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. DESCRIPTION OF AUTOCLAVES

Three AISI Type 304 stainless steel rocking autoclaves were used in the tests. The internal dimensions are 2-1/16 inches by 32 inches in depth. The wall thickness is 1-1/8 inches. All three of the autoclaves were hydrostatically tested cold at 18,000 psi. The electrical heating jackets are wired in two sections, top and bottom, and are individually controllable. Each autoclave is provided with a rupture disc for safety. The rocker mechanisms are driven by air motors. An electric timer actuates the rocker mechanism through a solenoid valve in the air line. Rocking of the autoclaves occurs for one 2-minute period every 2 hours. The autoclaves move through an arc of 85 degrees, starting at 35 degrees from the vertical, about 18 times per minute.

Figure 5 is a photograph of the autoclaves. A more detailed description of the autoclaves and operational procedures is given in MND-E-2145, Martin-ANPP Corrosion Testing Program; Methods and Procedures, February 1961.

B. EXPERIMENTAL PROGRAM

An initial investigation of several possible test programs led to the selection of a statistically designed experiment. One of the many outstanding advantages of a designated experiment is the inherent ability to determine main effects and interaction effects of the independent variables with assurance. It is nearly impossible to determine the latter with any other type of experiment. The factorial design lends itself readily not only to mathematical evaluation but also to graphic presentation of the results.

1. Outline of Designed Experiment

a. Purpose

The basic purpose of the designed experiment was to determine the relative resistance of Monel and nickel to general corrosion under various environmental conditions. In addition, a few incidental tests with Inconel were planned for comparison.

The test specimens were also to be examined for pitting, cracking and other evidence of local attack. However, these factors entered into the statistical analysis only to the extent that they affected the weight loss due to corrosion.
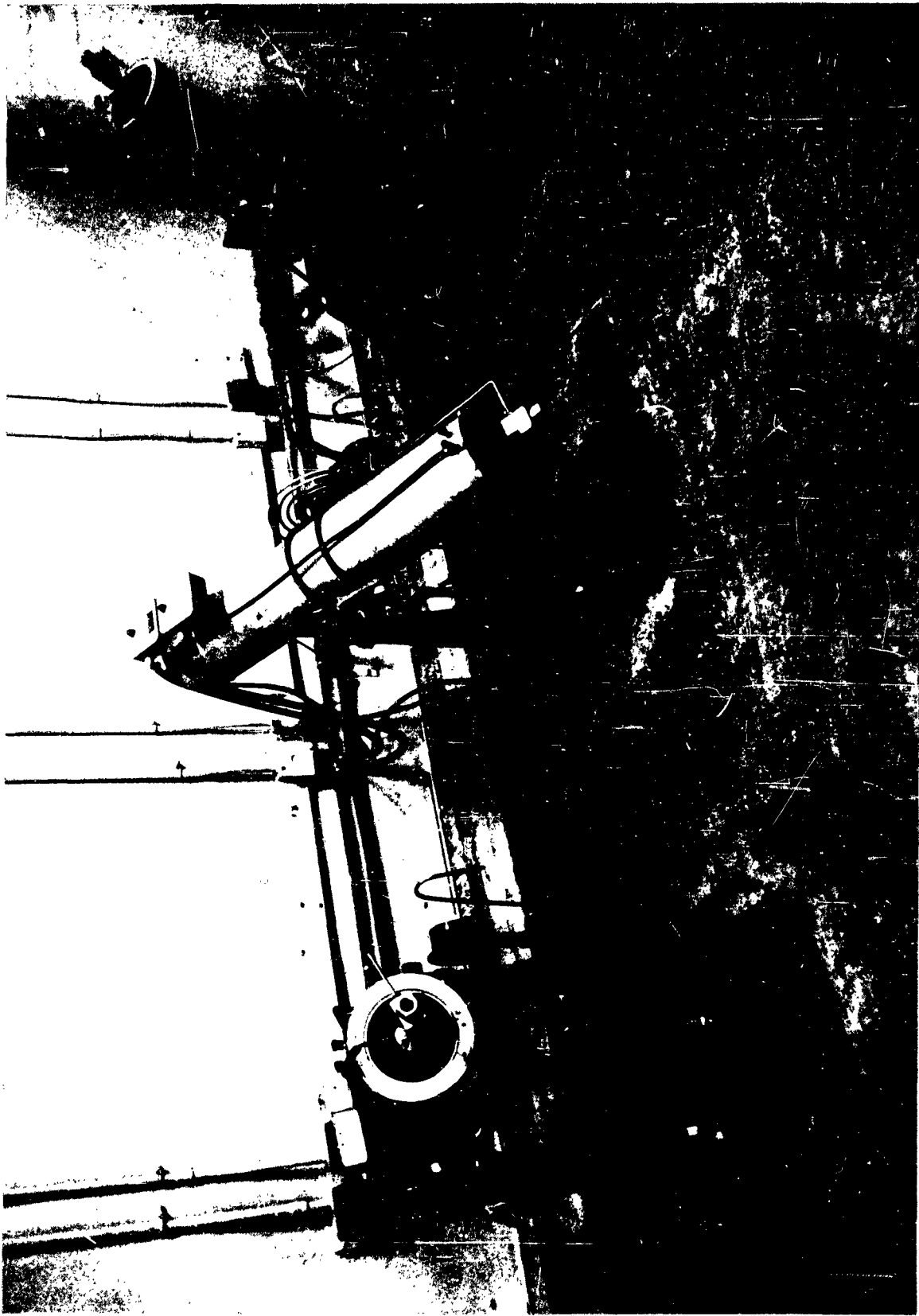
Fig. 5. Rocking Autoclaves

b. Experimental factors

There were eight experimental factors. Each factor had two levels, except chloride and time, which had three. These were:

Factors	Levels
Material	Monel and nickel
Chloride	10 ppm, 100 ppm and 1000 ppm
Alkalizing agent (pH 10)	Na_3PO_4 and NaOH
Oxygen*	Low (~1 ppm) and high (~15 ppm)
Heat treatment	Annealed and stress-relieved
Stress level	Unstressed and stressed to 90% yield
Phase	Vapor and liquid
Time	50, 200 and 2000 hours

*The initial concentration of oxygen dissolved in the water at operating temperature.

c. Experimental design

Three autoclaves, randomly assigned, were used for the experiment. Chloride, oxygen and pH adjustment were the conditions imposed within each autoclave. In the block diagram shown in Fig. 6, these factors and the materials are the column factors. There were three row factors: heat treatment, stress level and phase. The two classes of each row factor were run simultaneously within an autoclave and three specimens were exposed at each set of conditions. Thus, 24 coupons were exposed in each autoclave run. This procedure ruled out fractionalizing the replicates among the row factors. Also, because of information losses, particularly concerning possible interactions, a fractional factorial was not considered.

The test program indicated by Fig. 6 was employed for the 200-hour tests. Since each column in Fig. 6 represents one test run, this series consisted of 24 runs.

Tests were also performed for 50- and 2000-hour durations to investigate the temporal behavior of the corrosion rate. The test programs

Fig. 6. Autoclave Test Program--200 Hours

Column structure (all data cells empty):

Monel / Nickel

- Monel: Cl_1, Cl_2, Cl_3
- Nickel: Cl_1, Cl_2, Cl_3

Each Cl divided into pH_1, pH_2; each pH divided into O_1, O_2.

Row structure:

HT$_1$	S	V
		L
	U	V
		L
HT$_2$	S	V
		L
	U	V
		L
Total		

			Nickel				Monel			
			Cl_3		Cl_1		Cl_3		Cl_1	
			O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1
HT_1	S	V								
		L								
	U	V								
		L								
HT_2	S	V								
		L								
	U	V								
		L								
Total										

Fig. 7. Autoclave Test Program--50 Hours

		Monel		Nickel		Inconel	
		Cl_1 O_1	Cl_3 O_2	Cl_1 O_1	Cl_3 O_2	Cl_1 O_1	Cl_3 O_2
HT_1	S	V					
		L					
	U	V					
		L					
HT_2	S	V					
		L					
	U	V					
		L					
Total							

Fig. 8. Autoclave Test Program--2000 Hours

for each exposure time are indicated in Figs. 7 and 8. Table 4 defines the symbols used in Figs. 6, 7 and 8.

For all tests, the primary result was weight loss due to corrosion. The weight of each specimen was determined prior to exposure by an analytic balance. After exposure, the corrosion film was stripped off, using an appropriate descaling technique (see Section IV-C). Again, the weight was determined by the same balance and operator as previously. Weight loss data was corrected for attack of the base metal by the descaling agents (blank corrections).

TABLE 4

Definition of Symbols Used in Figs. 6, 7 and 8

Symbol	Definition
Cl_1	10 ppm chloride
Cl_2	100 ppm chloride
Cl_3	1000 ppm chloride
O_1	1 ppm oxygen
O_2	15 ppm oxygen
pH_1	NaOH
pH_2	Na_3PO_4
HT_1	Annealed
HT_2	Stress-relieved
S	Stressed
U	Unstressed
V	Vapor phase
L	Liquid phase

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C. WEIGHT LOSS DETERMINATION--DESCALING TECHNIQUES

Many methods were evaluated in an effort to find an acceptable descaling process. These methods included: (1) cathodic treatment in 5% sulfuric acid inhibited with 0.8 gm/l ethylquinolinium iodide, followed by a dip in 10% nitric acid or 10% ammonium hydroxide; (2) a treatment in boiling 25% sulfamic acid for one hour; (3) an alkaline permanganate (10% NaOH-5% $KMnO_4$) and 10% oxalic acid process; and (4) cathodic treatment in 10% caustic solution, followed by a dip in 10% nitric acid.

The descaling method concluded to be the best for Monel and nickel coupons was the sulfamic acid bath. This treatment consisted of exposing the corroded coupons to boiling 25% sulfamic acid for one hour. After removal from the descaling bath, the coupons were rinsed in water, rinsed in acetone, then dried with an electrically heated blower. The blank correction is 2.3×10^{-5} gm/cm^2. Although this blank correction was in some cases close to the oxide weight, it was considerably lower than the correction of any other method evaluated.

The descaling method concluded to be the best for Inconel was the alkaline permanganate-oxalic acid procedure. This treatment consisted of exposing the corroded coupons to an alkaline permanganate solution to loosen the oxide, followed by exposure to 10% oxalic acid solution. The blank correction is 4.3×10^{-5} gm/cm^2.

D. TEST PROCEDURES

In general, the test procedures were established so that all coupons and autoclaves were treated in identical fashion, except for the desired variation in experimental factors.

Prior to each test run, the three autoclaves and accompanying high pressure tubing were rinsed with acetone and then rinsed with hot distilled water until the silver nitrate test for chloride was negative. Finally, they were rinsed with demineralized water of one million ohm-centimeter resistivity.

Immediately prior to mounting the test specimens on the holders, the coupons were rinsed in acetone, pickled in 1:1 hydrochloric acid to remove all surface contamination, rinsed with demineralized water, dried with an electrically heated air blower and weighed.

Stock solutions of all the water treatment chemicals for use throughout the program were prepared prior to any autoclave testing. These included N/10 $Na_3PO_4 \cdot 12 H_2O$, N/10 NaOH and a large supply of NaCl

solution from which aliquot portions were withdrawn and properly diluted in volumetric glassware to produce the 10 ppm, 100 ppm and 1000 ppm Cl solutions. The Na_3PO_4 solution used to adjust the pH was back titrated with enough Na_2HPO_4 to assure that there was no free alkali in the solution. Deionized water was used in the preparation of all solutions.

Two specimen holders and the required solution were loaded into each autoclave. One holder occupied the liquid phase of the autoclave and the other, the vapor. The concentration of oxygen (1 or 15 ppm) was defined as the oxygen dissolved in the water at operating temperature and pressure. For those tests which required high oxygen (15 ppm), the autoclaves were half filled with the test solution and sealed in air. For those tests which required low oxygen (1 ppm), the autoclaves were half filled with the test solution and the pressure was reduced to 5.4 inches of mercury, maintained for half an hour and sealed. Separate autoclave tests were run to determine the concentration of oxygen at temperature in the water when the autoclaves were set up as described above.

After sealing, the autoclaves were brought up to the required temperature and pressure (450° F and 422 psia, respectively). An automatic timer was set for the required test duration. The test runs were automatically terminated and, after a cooling period, the autoclaves were opened.

Immediately following removal from the autoclave, the coupons were rinsed in demineralized water, dried, weighed, inspected with a 30-power binocular microscope, descaled, weighed and reinspected with a 30-power binocular microscope. X-ray diffraction was used directly on some representative corrosion films. Photomicrographs were made of selected coupons. Finally, the specimens were stored in a manner which prevented further deterioration.

V. TEST OBSERVATIONS

A. WEIGHT LOSS DATA

The dependent variable (also referred to as the observed value or the response) was, in all tests, the weight loss of metal from the coupon by corrosion. The tests were performed in three groups according to length of time in the saturated water environment at a temperature of 450° F. The time intervals were 50, 200 and 2000 hours.

The effects on the corrosion process of as many as eight different independent variables were examined. The independent variables, together with the levels or values of each, that were investigated were: (1) oxygen concentration--1 and 15 ppm (nominal); (2) chloride concentration--10, 100 and 1000 ppm; (3) method of pH control--NaOH and Na_3PO_4; (4) phase in which coupon was immersed--vapor and liquid; (5) stress on the coupon--stressed and unstressed; (6) method of heat treatment used on the coupon--annealed and stress relieved; (7) metal of which the coupon was made--nickel, Monel and Inconel; and (8) the time interval--50, 200 and 2000 hours.

For purposes of analysis, the test runs were considered to comprise four complete factorial experiments*; one at each of the three time intervals and a fourth, with time included as an independent variable. The 50-hour experiment was a complete 2^6 factorial, in which Na_3PO_4 was used exclusively for pH control. The six independent variables, each of which was investigated at two levels, were: (1) oxygen, (2) chloride, (3) metal, (4) phase, (5) stress, and (6) heat treatment. The levels of chloride were 10 and 1000 ppm, and the two metals were nickel and Monel. The observed values are shown in Table 5. In this experiment, and throughout the entire program, each treatment combination was replicated three times (repeated twice).

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* In a complete factorial experiment all combinations of all the values, or levels, of all the independent variables, or factors, are tested. Each particular combination is called a treatment combination. In describing a complete factorial experiment it is customary to refer to its number of treatment combinations. Thus, if it consists of three factors, the first examined at "a" levels, the second at "b" levels, and the third at "c" levels, it is an a x b x c factorial. Or, if there are "h" factors and each factor is examined at "g" levels, it is a g^h factorial.

The 200-hour experiment was a 2^6 x 3 factorial. The six independent variables investigated at two levels each were: (1) oxygen, (2) pH control, (3) phase, (4) stress, (5) heat treatment, and (6) metal. The two levels of metal were nickel and Monel. The independent variable investigated at three levels was chloride. The responses are presented in Table 6.

The 2000-hour experiment was a 2^4 x 3 factorial. In this experiment the oxygen and chloride concentrations were combined into one independent variable, the lower level of which was 1 ppm O_2, 10 ppm Cl, and the upper level of which was 15 ppm O_2, 1000 ppm Cl. The four independent variables at two levels each were: (1) chloride-oxygen, (2) phase, (3) stress, and (4) heat treatment. The three-level independent variable was metal--Monel, nickel and Inconel. The method of pH control for this experiment was Na_3PO_4. The data appear in Table 7.

The fourth complete factorial was a 2^5 x 3. The same combined chloride-oxygen independent variable of the 2000-hour experiment was employed again. The five independent variables investigated at two levels each were: (1) chloride-oxygen, (2) phase, (3) stress, (4) heat treatment, and (5) metal. The two metals were nickel and Monel. The three-level independent variable was time. The pH control was Na_3PO_4, exclusively. The data, which consist of values extracted from Tables 5 through 7, are combined in Table 8.

Photographs of specimens and holders as they appeared upon removal from the autoclaves are shown in Figs. 9 and 10.

X-ray diffraction tests were performed on the corrosion films from a number of representative coupons. In all cases, the principal constituent was gamma nickel hydroxide, NiOOH.

B. INCIDENCE OF CRACKING AND PITTING CORROSION

The results of these autoclave tests confirmed that, under the varied and severe test conditions used, nickel, Monel and Inconel are not susceptible to stress corrosion cracking and they are very resistant to corrosion. An incipient surface attack was noted on some of the Monel and nickel specimens that were tested for 50 and 200 hours, but none of the specimens cracked or pitted. No cracking of any coupons was observed in the 2000-hour autoclave test, but varying degrees of attack and some pitting did occur.

TABLE 5

50-Hour Test--Weight Loss From Corrosion (mg)

			Nickel				Monel			
			Cl_1		Cl_3		Cl_1		Cl_3	
			O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2
Annealed	Stressed	V	1.4	0.7	2.1	2.3	0.0	0.6	0.3	1.0
			0.9	0.9	1.7	2.6	0.0	0.3	0.1	1.5
			1.0	0.8	1.2	2.6	0.2	0.5	0.0	0.8
		L	0.4	1.1	0.5	0.5	1.5	0.1	0.0	0.1
			0.7	0.6	0.3	0.6	0.3	0.1	0.0	0.2
			0.6	0.9	0.3	0.3	0.2	0.4	0.0	0.4
	Unstressed	V	1.1	1.0	1.8	2.5	0.1	0.3	0.0	1.5
			0.8	1.3	1.7	2.6	0.0	0.4	0.1	1.4
			0.7	0.6	1.7	2.4	0.3	0.4	0.3	2.5
		L	0.5	1.1	0.4	0.6	0.2	0.1	0.0	0.0
			0.4	1.1	0.1	0.5	0.4	0.3	0.0	0.1
			0.4	0.7	0.0	0.2	0.2	0.0	0.2	0.0
Stress-Relieved	Stressed	V	1.3	1.6	1.5	2.2	0.7	0.7	0.2	1.4
			1.2	3.0	1.5	2.1	0.5	0.7	0.1	2.0
			1.2	1.8	1.6	1.5	0.5	0.3	0.2	1.5
		L	0.4	1.3	1.3	0.6	0.6	0.3	0.4	0.7
			0.6	1.5	1.2	0.8	0.0	0.0	0.2	0.9
			0.6	2.0	1.1	1.0	0.2	0.5	0.3	0.8
	Unstressed	V	1.3	1.8	1.8	2.0	0.7	0.3	0.2	2.1
			1.5	2.6	1.8	2.3	0.6	0.5	0.2	2.4
			0.9	1.6	1.9	2.3	0.7	0.6	0.5	1.8
		L	0.7	1.8	0.7	1.2	0.2	0.2	0.3	0.6
			0.4	2.0	1.3	1.4	0.4	0.5	0.2	0.6
			0.6	2.1	1.1	1.0	0.3	0.3	0.0	0.8

TABLE 6

200-Hour Test--Weight Loss from Corrosion (mg)

Nickel

			Cl_1				Cl_2				Cl_3			
			pH_1		pH_2		pH_1		pH_2		pH_1		pH_2	
			O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2
Annealed	Stressed	V	1.4	1.7	--	1.7	0.8	0.6	0.8	0.8	2.6	0.7	5.2	3.4
			1.3	1.3	0.5	1.3	1.0	0.5	1.2	1.2	1.9	0.6	3.1	1.4
			1.3	1.2	0.3	1.3	1.0	1.3	0.9	1.4	1.0	0.7	1.8	2.1
		L	0.9	1.5	0.6	1.7	0.8	0.9	1.3	1.6	1.8	0.2	2.1	3.0
			1.5	0.5	1.0	1.3	0.7	1.0	0.9	1.4	1.1	0.6	1.6	2.7
			1.5	1.3	0.4	1.3	1.1	1.1	1.3	1.9	1.0	0.6	1.0	2.0
	Unstressed	V	1.4	1.5	0.5	1.0	0.3	0.8	0.7	1.3	1.8	1.0	2.1	1.5
			1.4	0.9	0.6	1.1	0.6	0.7	1.3	1.4	2.1	0.6	2.6	1.0
			1.2	1.5	0.4	1.2	0.9	0.8	0.7	1.4	1.9	1.0	2.4	1.9
		L	1.6	1.5	0.8	1.3	0.6	1.0	1.6	1.5	1.5	0.7	0.9	2.2
			1.5	1.3	0.5	0.7	0.4	0.9	1.8	1.6	1.3	0.8	1.4	1.6
			1.2	1.2	--	1.1	0.6	0.8	1.4	1.4	0.9	0.6	0.8	1.9
Stress-Relieved	Stressed	V	0.9	1.7	--	1.6	1.1	1.1	1.4	1.2	2.0	2.2	2.4	2.6
			2.4	1.5	0.7	1.3	0.8	0.7	1.6	1.9	2.3	2.7	2.4	2.7
			4.4	1.2	0.9	1.5	1.4	1.5	0.8	1.4	2.1	1.4	2.4	2.2
		L	2.2	1.3	0.7	2.6	1.0	0.9	1.5	1.1	1.5	0.9	1.1	3.1
			2.3	1.4	1.0	0.9	0.7	1.1	1.6	1.4	1.2	0.7	1.4	2.0
			2.1	0.6	1.1	1.7	0.7	0.6	1.4	1.2	1.3	0.5	1.0	3.1
	Unstressed	V	2.2	1.5	0.4	0.7	1.0	1.0	1.1	1.3	1.9	2.0	3.8	2.6
			2.2	1.6	0.4	1.4	1.6	1.0	0.7	1.5	2.1	1.7	2.7	2.8
			2.0	1.5	0.5	1.4	1.2	0.9	1.1	1.7	2.3	1.3	1.9	2.0
		L	2.3	1.8	0.8	1.4	0.9	0.9	1.0	1.5	1.7	0.8	1.1	2.3
			2.3	1.6	0.8	1.1	0.9	0.6	0.9	1.3	1.3	0.8	1.3	0.6
			1.2	0.9	--	1.8	0.6	1.3	0.6	0.7	1.1	0.5	1.4	1.2

TABLE 6 (continued)

Monel

			Cl_1				Cl_2				Cl_3			
			pH_1		pH_2		pH_1		pH_2		pH_1		pH_2	
			O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2
Annealed	Stressed	V	0.8	2.1	1.3	0.9	0.8	1.5	--	1.1	0.7	4.1	1.3	6.8
			0.2	2.2	1.0	0.7	0.6	0.6	1.4	1.0	0.6	3.9	0.6	6.1
			0.6	2.5	1.9	0.5	0.7	1.1	1.3	1.4	0.4	3.6	0.9	5.0
		L	0.6	1.3	1.7	0.8	0.6	1.0	1.4	1.3	0.4	3.3	0.6	2.5
			0.8	1.0	0.8	0.8	0.7	1.1	1.3	1.0	0.5	3.4	0.0	1.8
			0.4	1.5	1.1	0.6	0.5	0.7	1.3	1.5	0.2	3.8	0.7	2.2
	Unstressed	V	0.2	1.6	1.0	0.8	0.4	1.0	0.9	1.3	0.5	3.8	0.3	6.3
			0.5	2.4	1.3	0.9	0.3	1.2	1.4	1.4	0.6	4.1	1.1	6.5
			0.0	3.7	1.1	0.5	0.5	1.2	1.4	1.4	0.9	4.3	0.0	5.3
		L	0.2	1.4	1.3	1.2	0.6	0.7	1.3	1.4	0.4	3.6	0.6	2.0
			0.2	1.0	1.6	0.7	0.5	1.1	1.4	1.0	0.6	3.4	0.0	3.1
			0.4	1.3	1.4	1.0	0.3	1.0	--	1.3	0.3	3.1	0.7	2.1
Stress-Relieved	Stressed	V	0.6	1.9	2.1	0.8	0.5	2.0	--	0.7	1.0	1.9	2.7	3.6
			0.5	2.3	2.5	0.7	0.5	1.1	1.1	1.3	0.7	5.2	0.7	5.6
			0.0	2.6	2.6	0.8	0.6	1.1	1.3	1.7	0.9	4.1	1.1	4.2
		L	0.2	1.2	1.8	0.5	0.7	0.9	0.8	1.1	0.6	4.0	1.2	3.3
			0.2	1.2	1.3	0.9	1.0	1.4	0.9	0.8	0.3	3.2	1.2	1.5
			0.3	1.0	1.6	1.7	0.4	1.2	0.8	0.8	0.5	3.5	0.9	1.6
	Unstressed	V	0.4	2.1	2.9	1.0	0.5	0.9	1.1	1.3	0.9	4.6	0.9	4.4
			0.3	1.9	2.5	0.5	0.1	2.4	0.8	1.4	0.7	4.5	0.9	5.4
			0.2	2.5	1.9	1.9	0.5	1.5	0.9	1.2	0.5	3.9	0.3	4.5
		L	0.2	1.5	1.8	0.9	0.6	1.9	1.2	0.9	0.7	3.6	0.7	2.0
			0.2	1.3	1.2	0.5	0.8	1.3	1.0	0.9	0.6	3.6	1.0	1.7
			0.2	1.7	0.8	0.6	0.6	1.2	--	0.7	0.4	1.1	1.0	1.2

TABLE 7

2000-Hour Test--Weight Loss from Corrosion (mg)

			Nickel		Monel		Inconel	
			Cl_1	Cl_3	Cl_1	Cl_3	Cl_1	Cl_3
			O_1	O_2	O_1	O_2	O_1	O_2
Annealed	Stressed	V	7.0	5.3	5.7	7.8	0.1	0.0
			5.9	5.2	11.6	7.1	0.1	0.0
			6.8	4.0	9.2	6.3	0.0	0.0
		L	6.7	2.4	11.6	6.2	0.0	0.3
			6.1	4.5	9.4	7.0	0.0	0.0
			4.6	4.6	12.9	5.8	0.0	0.1
	Unstressed	V	4.9	6.1	11.1	8.6	0.0	0.0
			3.7	6.5	10.5	8.8	0.0	0.0
			6.1	4.7	10.7	8.3	0.0	0.0
		L	7.1	3.2	7.3	6.1	0.0	0.0
			8.4	3.3	9.2	6.9	0.0	0.0
			6.7	4.1	14.0	7.2	0.0	0.1
Stress-Relieved	Stressed	V	10.6	4.1	9.4	8.6	0.4	0.7
			6.8	4.9	7.9	--	0.9	0.4
			9.1	3.3	6.4	9.9	0.8	1.1
		L	7.6	12.8	6.2	7.8	1.4	1.2
			7.6	8.3	9.0	--	1.6	1.1
			5.4	1.8	9.5	4.1	1.1	1.1
	Unstressed	V	6.5	4.7	7.8	8.1	1.0	0.3
			4.7	6.6	10.9	--	0.7	0.6
			10.6	4.2	6.7	9.9	0.6	0.6
		L	6.1	1.9	5.9	8.9	1.4	1.2
			6.9	1.1	6.1	--	2.2	0.9
			5.2	7.3	8.3	6.4	1.4	1.0

TABLE 8

Combined 50-, 200- and 2,000-Hour Test-- Weight Loss from Corrosion (mg)

			50 hr Nickel Cl_1 O_1	50 hr Nickel Cl_3 O_2	50 hr Monel Cl_1 O_1	50 hr Monel Cl_3 O_2	200 hr Nickel Cl_1 O_1	200 hr Nickel Cl_3 O_2	200 hr Monel Cl_1 O_1	200 hr Monel Cl_3 O_2	2000 hr Nickel Cl_1 O_1	2000 hr Nickel Cl_3 O_2	2000 hr Monel Cl_1 O_1	2000 hr Monel Cl_3 O_2
Annealed	Stressed	V	1.4	2.3	0.0	1.0	--	3.4	1.3	6.8	7.0	5.3	5.7	7.8
			0.9	2.6	0.0	1.5	0.5	1.4	1.0	6.1	5.9	5.2	11.6	7.1
			1.0	2.6	0.2	0.8	0.3	2.1	1.9	5.0	6.8	4.0	9.2	6.3
	Stressed	L	0.4	0.5	0.5	0.1	0.6	3.0	1.7	2.5	6.7	2.4	11.6	6.2
			0.7	0.6	0.3	0.2	1.0	2.7	0.8	1.8	6.1	4.5	9.4	7.0
			0.6	0.3	0.2	0.4	0.4	2.0	1.1	2.2	4.6	4.6	12.9	5.8
	Unstressed	V	1.1	2.5	0.1	1.5	0.5	1.5	1.0	6.3	4.9	6.1	11.1	8.6
			0.8	2.6	0.0	1.4	0.6	1.0	1.3	6.5	3.7	6.5	10.5	8.8
			0.7	2.4	0.3	2.5	0.4	1.9	1.1	5.3	6.1	4.7	10.7	8.3
	Unstressed	L	0.5	0.6	0.2	0.0	0.8	2.2	1.3	2.0	7.1	3.2	7.3	6.1
			0.4	0.5	0.4	0.1	0.5	1.6	1.6	3.1	8.4	3.3	9.2	6.9
			0.4	0.2	0.2	0.0	--	1.9	1.4	2.1	6.7	4.1	14.0	7.2
Stress-Relieved	Stressed	V	1.3	2.2	0.7	1.4	0.8	2.6	2.1	3.6	10.6	4.1	9.4	8.6
			1.2	2.1	0.5	2.0	0.7	2.7	2.5	5.6	6.8	4.9	7.9	--
			1.2	1.5	0.5	1.5	0.9	2.2	2.6	4.2	9.1	3.3	6.4	9.9
	Stressed	L	0.4	0.6	0.6	0.7	0.7	3.1	1.8	3.3	7.6	12.8	6.2	7.8
			0.6	0.8	0.0	0.9	1.0	2.0	1.3	1.5	7.6	8.3	9.0	--
			0.6	1.0	0.2	0.8	1.1	3.1	1.6	1.6	5.4	1.8	9.5	4.1
	Unstressed	V	1.3	2.0	0.7	2.1	0.4	2.6	2.9	4.4	6.5	4.7	7.8	8.1
			1.5	2.3	0.6	2.4	0.4	2.8	2.5	5.4	4.7	6.6	10.9	--
			0.9	2.3	0.7	1.8	0.5	2.0	1.9	4.5	10.6	4.2	6.7	9.9
	Unstressed	L	0.7	1.2	0.2	0.6	0.8	2.2	1.8	2.0	6.1	1.9	5.9	8.9
			0.4	1.4	0.4	0.6	0.8	0.6	1.2	1.7	6.9	1.1	6.1	--
			0.6	1.0	0.3	0.8	--	1.2	0.8	1.2	5.2	7.3	8.3	6.4

Vapor phase

Water phase
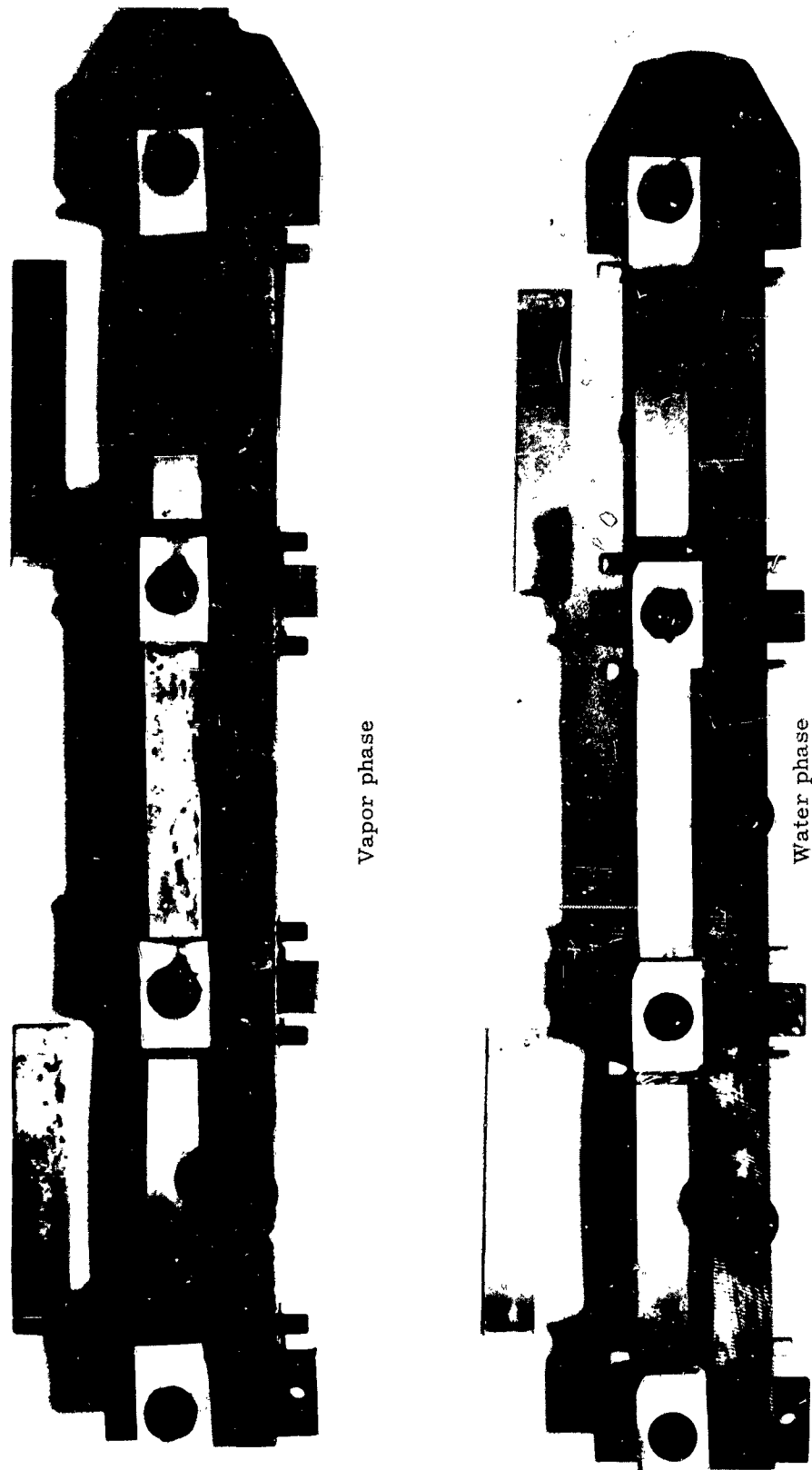
Fig. 9. Nickel Specimens Autoclaved at 450° F for 200 Hours in 1000 ppm Cl, 15 ppm Dissolved O_2, and pH Adjusted to 10 with Na_3PO_4

Vapor phase

Water phase

Monel
1000 ppm Cl
15 ppm O_2
pH 10 - Na_3PO_4
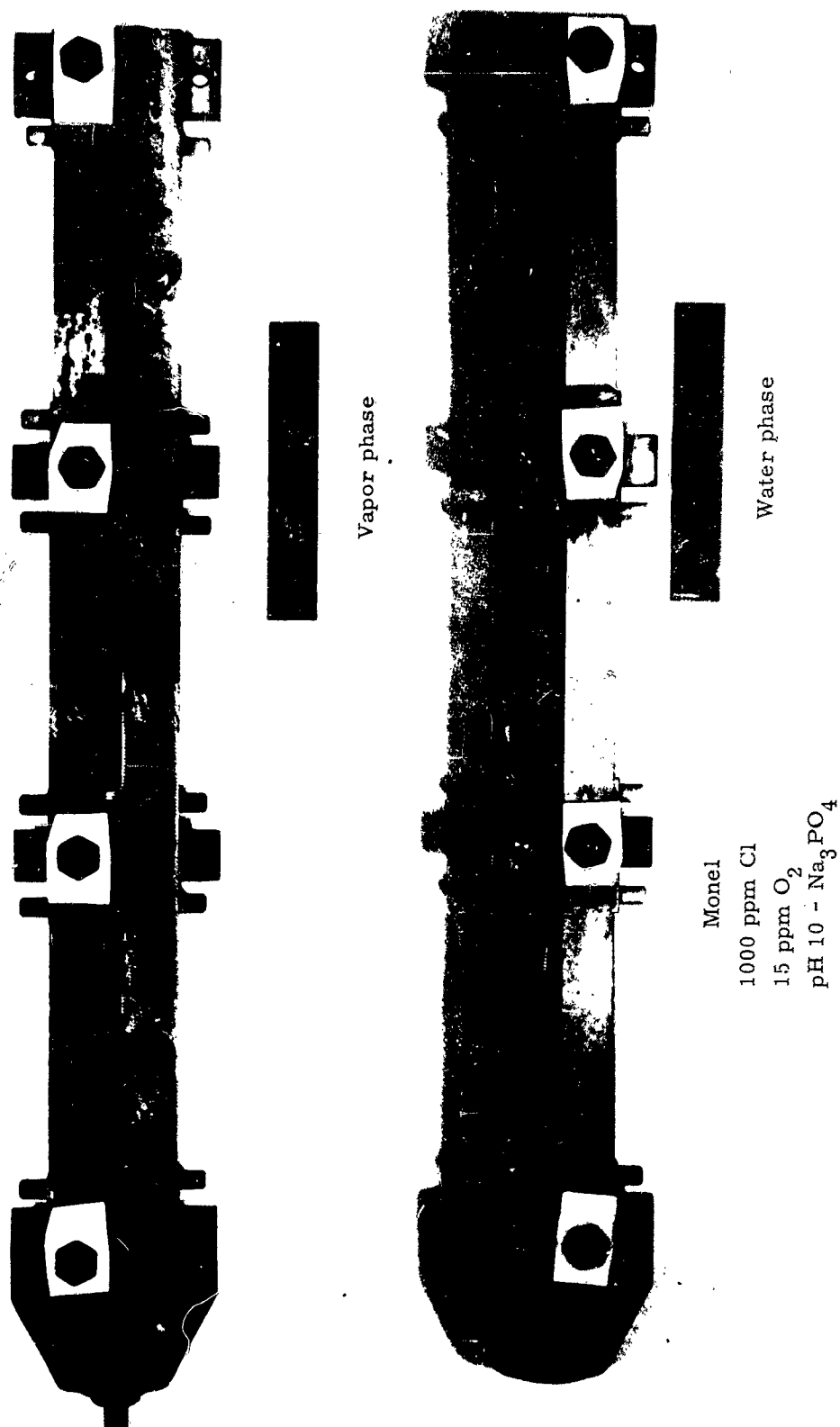
Fig. 10. Appearance of Monel Coupons as Removed from Autoclave

The coupons from the 2000-hour test presented a more meaningful appearance than those from the previous shorter tests because there is a definite criterion for direct visual comparison. The Monel vapor phase specimens exposed to high chloride-high oxygen pitted mildly, as shown in Fig. 11. All 12 of the vapor phase coupons and none of the liquid phase coupons suffered attack. No significant difference in attack was noted between stressed and unstressed coupons or between annealed and stress-relieved coupons. The attack occurred on both the tension and compression surfaces of the coupons. The macrophotograph of one of the specimens (Fig. 11) illustrates the extent of attack quite well. The affected areas were relatively large but shallow, with the average depth about 1 mil. Frequently, a centrally located pit with a diameter-to-depth ratio of about 2 was surrounded by an area of shallow attack which was, perhaps, 50 to 60 mils in diameter. In some instances, more than one pit occurred in the area of attack. The maximum penetration measured was 1.5 mils. A photomicrograph of a typical pit is shown in Fig. 12. No pitting or attacked areas occurred on the Monel coupon in either the vapor or liquid phase in the low chloride-low oxygen test.

The nickel coupons exposed to vapor in the 2000-hour, high chloride-high oxygen test were attacked mildly, as shown in Fig. 13. Both the tension and the compression surfaces were affected, but the tension surface was worse. There was a slightly greater attack on the stress-relieved coupons than on the annealed coupons. The liquid phase coupons were attacked also, but very slightly. The pits in most cases were hardly more than incipient attack. Four of the 12 specimens were pitted; the maximum depth found was 0.5 mil. Coupons in the low chloride-low oxygen test were also pitted. Five of the 12 vapor phase coupons were attacked. One coupon has only three pits but the other four had perhaps 200 pits per square inch. The physical condition of the specimen (heat treatment and stress) appeared to have no effect on pitting. Five of the 12 water phase specimens were also pitted. They, too, were liberally covered with pits. The appearance of pits on both vapor and water-phase coupons contrasted sharply with the previously noted shallow attack on Monel coupons. The ratio of diameter to depth was about 2; however, there was no surrounding area of attack. The maximum depth found was 1.5 mils. A photomicrograph is shown in Fig. 14.

Half of the Inconel vapor phase coupons in the high chloride-high oxygen test showed very shallow attack as shown in Fig. 15. An isolated pit found on one of the coupons was 4 mils deep, but generally the pits were no deeper than about 1 mil. The attack occurred on both the tension and compression surfaces of the coupons and appeared to be about evenly divided, so far as heat treatment and stress were concerned. A photomicrograph of a typical pit is shown in Fig. 16. No attack was noted on the coupons in vapor or liquid phases of the low chloride-low oxygen test.
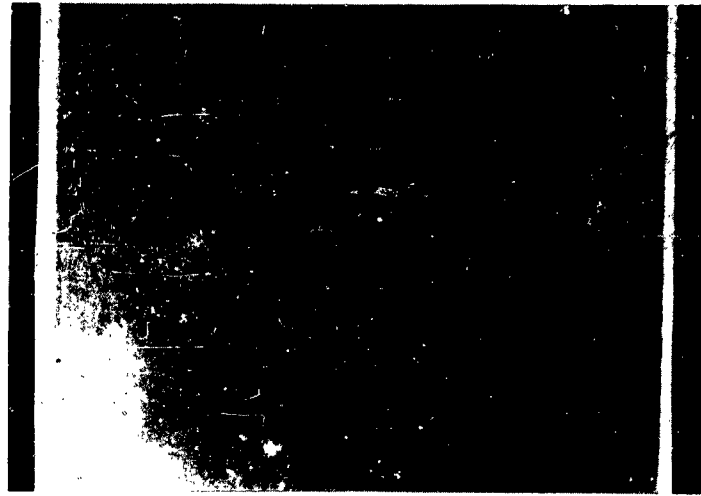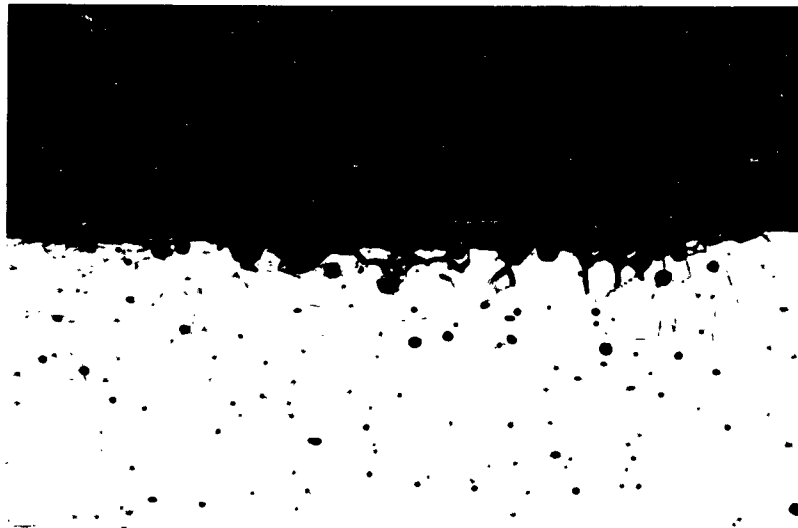
1000 ppm Cl   pH 10 (Na$_3$ PO$_4$)
15 ppm O$_2$
                     2000-hr exposure
Vapor phase

Fig. 11. Portion of Monel Coupon Showing Incidence of Pitting
(6.5x magnification)

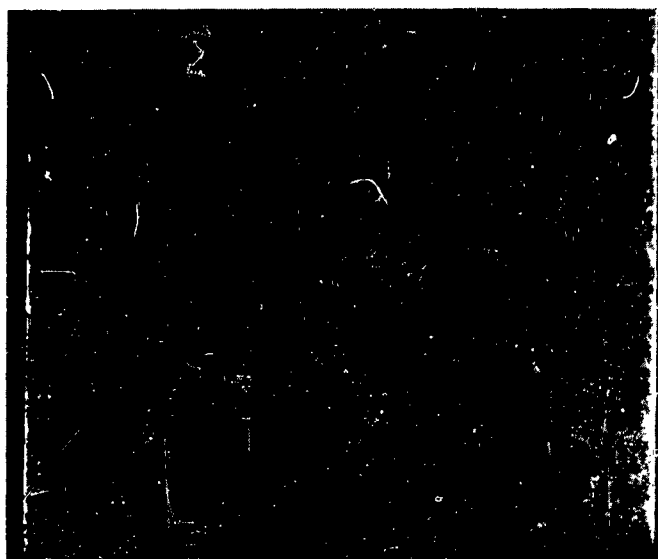
1000 ppm Cl   pH 10 (Na$_3$PO$_4$)
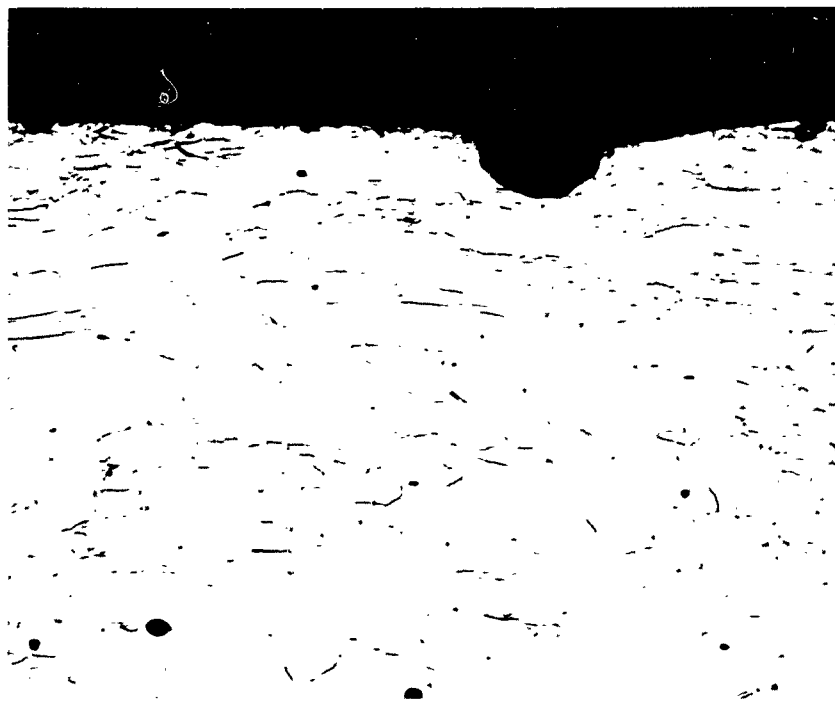15 ppm O$_2$
                     2000-hr exposure
Vapor phase

Fig. 12. Photomicrograph of Monel Specimen Showing
0.0014-Inch Deep Pit (250x magnification)

36

1000 ppm Cl   pH 10 (Na$_3$PO$_4$)
15 ppm O$_2$
Vapor phase   2000-hr exposure

Fig. 13. Portion of Nickel Coupon (6.5x Magnification)

1000 ppm Cl   pH 10 (Na$_3$PO$_4$)   0.00035-in. penetration (max)
15 ppm O$_2$
Vapor phase   2000-hr exposure

Fig. 14. Photomicrograph of Nickel Specimen Showing Pit
(750x Magnification)

1000 ppm Cl   pH   10 (Na_3PO_4)
15   ppm O_2 2000-hr exposure
Vapor phase

Fig. 15. Portion of Inconel Coupon (6.5x magnification)
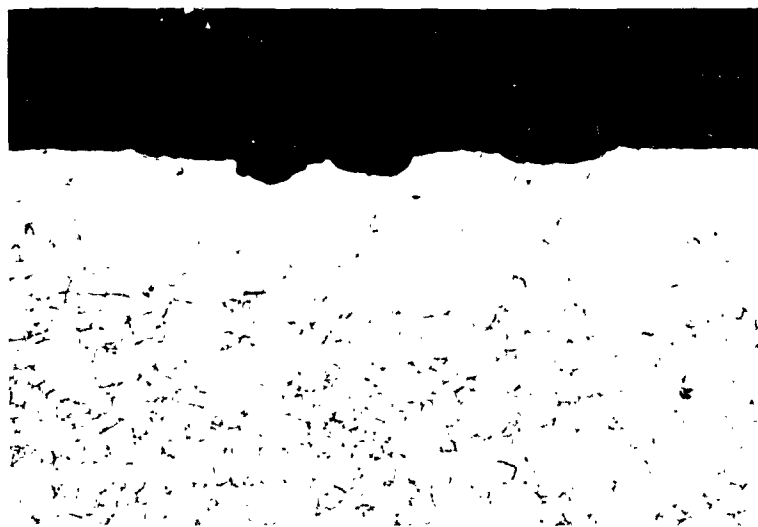
1000 ppm Cl   pH 10 (Na_3PO_4)
15 ppm O_2 2000-hr exposure
Vapor phase

Fig. 16. Photomicrograph of Inconel Specimen Showing 0.0016-Inch
Deep Pit (125x magnification)

MND-E-2655

In summation, no cracking of any coupons was observed in 2000-hour tests but varying degrees of incipient attack and some pitting did occur on all three metals.

C. ENVIRONMENTAL CONDITIONS

The chemistry of the environmental solutions was established, as specified, at the beginning of each test and the test solutions were analyzed after each test. Typical analyses for the 200-hour tests are shown in Table 9. Generally, the post-test chloride concentrations are in good agreement with the pretest concentrations. Although the pH dropped in some cases, the drop was no greater than would normally be expected.

TABLE 9
Environmental Conditions

Test No.	Material Tested	Oxygen (ppm)	Chloride (ppm)	pH Adjusted to 10	Chloride After Test (ppm)	pH After Test
1	Nickel	1	10	NaOH	22	8.3
2	Nickel	15	100	Na_3PO_4	90	8.4
3	Nickel	15	1000	Na_3PO_4	993	7.65
4	Monel	1	100	NaOH	110	8.85
5	Monel	15	10	NaOH	14	9.5
6	Monel	1	10	Na_3PO_4	7	6.6
7	Monel	1	1000	NaOH	1033	8.2
8	Monel	15	1000	NaOH	1007	9.0
9	Nickel	1	100	NaOH	111	9.35
10	Nickel	1	100	Na_3PO_4	98	8.0
11	Monel	1	10	NaOH	11	7.1
12	Nickel	15	10	Na_3PO_4	7	7.2
13	Nickel	15	10	NaOH	14	9.85
14	Monel	1	1000	Na_3PO_4	1001	9.30
15	Monel	1	100	Na_3PO_4	102	8.5
16	Nickel	1	1000	Na_3PO_4	1041	7.0
17	Monel	15	1000	Na_3PO_4	988	7.2
18	Monel	15	100	Na_3PO_4	92	7.4
19	Nickel	1	10	Na_3PO_4	12	8.4
20	Monel	15	10	Na_3PO_4	11	7.6
21	Nickel	15	100	NaOH	101	7.8
22	Nickel	1	1000	NaOH	1022	7.1
23	Monel	15	1000	NaOH	1007	7.0
24	Nickel	15	1000	NaOH	1007	7.6

VI. ANALYSIS OF TEST RESULTS

A. ANALYSIS OF VARIANCE--GENERAL*

The general method chosen for analyzing the data was the analysis of variance. The complete factorial experiment is particularly amenable to this technique, and its use enabled the effects of the various factors on the observed levels of corrosion to be separated and evaluated. Since the method required the summing of a large quantity of data in many different ways, much of the work was programmed for the IBM-7090. The use of the machine saved time and also helped to avoid human mistakes, although the method itself is somewhat self-checking, inherently.

The triple replication (three coupons for each treatment combination) of the four factorial experiments allowed the variance within replicates to be determined in each of the four. The variance within replicates is a measure of the error or unassignable variation in the experiment. If all three replicate tests of each treatment combination produced identical weight losses by corrosion, the experiment would have been performed with a maximum of precision, and the error variance would be zero. Departure from this ideal results in a non-zero variance within replicates, and the degree of departure and the magnitude of the variance are proportional.

If the means of the three replicates of the different treatment combinations differ from one another, this variation between means is affected by the variation within the replicate measurements. It may, in addition, be affected because the levels of one or more of the controlled variables are different in the different sets of conditions. A variance can be calculated from the means. If no other factor is operating to cause a variation of the data than that included in the error variance, then the variance of the means is another estimate of the error variance. If the variance of the means includes some factor other than that affecting the error variance, the variance of the means includes the variance of this factor in addition to the error variance.

In general, the effect of a factor refers to the difference the factor makes in the response. Specifically, the main effects of a factor are defined to be the differences between the means of the observed quantity for each of the levels of that factor, when the means have

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*The remarks of this section are amplified in Refs. 16 and 17.

been obtained by averaging over all the levels of all of the other factors. Each mean obtained in this manner ignores the effects of the other independent variables; the difference in the means between any two levels of the factor in question (one of its main effects) is a measure of its effect on the observed quantity when changing from one level to the other. Thus, a factor examined at only two levels has one main effect, whereas a factor investigated at more than two levels has several main effects, e.g., if a factor has three levels, there are three main effects.

In determining the effects of a factor, another quantity called interaction is also of considerable importance. Interaction between two factors exists when the effect of one factor is different (in magnitude and/or sign) at different levels of the other. Such an interaction is referred to as a two-factor interaction. If the value of a two-factor interaction is different at different levels of a third factor, there exists a three-factor interaction, and so on.

To better illustrate the concepts of main effect and interaction, a simple example in which the observed values of an experiment depend on two factors, A and B will be considered. Assume that two values of each factor were investigated and that, therefore, the responses may be arranged in a two-way table as follows:

| | | Level of A | |
		Lower	Higher
Level of B	Lower	65	73
	Higher	72	71

Since, with B at the lower level, a change in A from its lower level to its higher, increases the response, whereas with B at the higher level, the effect of A is different, an interaction between A and B exists. The main effect of A in this case would be measured by the difference between the mean responses at the two levels of A: $72 - 68.5 = 3.5$. Similarly, the main effect of B is: $71.5 - 69 = 2.5$. The interaction of A and B is one-half the difference between the effects of A at each level of B: $1/2 \ [(71 - 72) - (73 - 65)] = -4.5$, or it may just as well be considered as one-half the difference between the effects of B at each level of A: $1/2 \ [(71 - 73) - (72 - 65)] = -4.5$. The coefficient one-half is introduced to keep the interaction on equal footing with the main effect.

Now consider a complete factorial in an experiment with two factors, A and B, at m and n levels, respectively, each treatment

combination being tested r times. The variance calculated from the means at each level of A, where the means have been obtained by averaging over all levels of B, will have $m-1$ degree of freedom. Furthermore, this variance will be an estimate of the variance due to A, σ_A^2, plus σ_o^2 / nr, where σ_o^2 is the error variance. In the computations of the analysis of variance, the variance of the means at each level of A is multiplied by nr in order to make the coefficient of σ_o^2 equal to unity. The variance, when multiplied in this way, is termed a mean square, and thus provides an independent estimate of σ_o^2 when σ_A^2 is zero.

Although σ_A^2 has been called a variance and is indeed calculated like one (the sum of squares divided by the degrees of freedom), it is not really a variance, since the effect of A is not random but rather is fixed by the arbitrary choice of the levels of A.

In order to determine whether a main effect or interaction really exists, the corresponding mean square is compared with the error variance in a statistical test. The test used is the F-test, and it provides a method for determining whether the ratio of the mean square to the error variance is larger than might be expected by chance if they had both been drawn from the same population (i.e., if they were both estimates of the same thing, namely σ_o^2). If the F-test shows a mean square, say that of A, to be significantly greater than the error variance, it can be inferred that changing the level of A affects the response.

The F-distribution has been tabulated for certain levels of significance. The significance level generally used is the 5% level. If the calculated ratio of the mean square to the error variance exceeds the tabulated value of F at the 5% level (choice of the proper F value from the table depends also on the numbers of degrees of freedom in the mean square and error variance), we conclude that the factor has a real effect, and runs a 5% risk of being wrong in this conclusion.

In performing an analysis of variance, it is necessary to distinguish between two main types of independent variables, or factors: qualitative and quantitative. A qualitative factor is one in which the different levels cannot be arranged in order of magnitude, whereas a quantitative factor can be arranged in order of magnitude. Examples of qualitative factors in these corrosion experiments are the metal, the method of pH control, the phase in which the coupon is immersed

and the method of heat treatment, since there are no a priori reasons for arranging the levels of these factors in a particular order. The concentrations of oxygen and chloride, the time of exposure and the stress imposed on the coupon (0 or 90% of the yield stress) are quantitative variables, since their values can be associated with points on a numerical scale.

When an analysis involving a quantitative factor is performed, it is usually of interest to consider the relationship between the observed values and the levels of the factor. If the functional form of this relationship is known ahead of time, it is merely required to estimate from the observations the empirical constants necessary to completely specify the function. Generally, however, this is not the case. But it is possible to approximate the relationship over a finite range of the independent variable by a polynomial of the form:

$$y = a + bx + cx^2 + dx^3 + \ldots$$

When the range of the factor is sufficiently narrow, only a few terms may be required to give an accurate enough representation.

If only two levels of the factor are investigated, a straight line is the only functional form that can be fitted uniquely, and it is tacitly assumed that, over the range considered, the desired relationship is linear to a sufficient degree of approximation. In the same way, when only three levels are used, a quadratic function is implied, and so on.

For a factor at two levels, the necessary computations are identical regardless of whether the factor is qualitative or quantitative. However, if a quantitative factor has been examined at three levels, it becomes possible to partition, or resolve, its main effect and interaction mean squares into linear and quadratic components, and to test each component for significance individually. The components of a mean square partitioned in this way algebraically sum to the total mean square of the main effect or interaction.

In interpreting the results of an analysis of variance, it is essential to consider them in light of the particular physical situation under investigation. However, a few general remarks are applicable. When the main effects of two factors are significant and their interaction is not, it is possible to make a general statement concerning the effect of each factor on the observed quantity.

However, when an interaction is large, the corresponding main effects fail to have much meaning. In the numerical example previously considered, the interaction between A and B is of the same order of magnitude as the main effects. It is of no advantage to know that the average response (i.e., averaged over both levels of B) for A at the higher level is greater than the average response for A at the lower level. The existence of a sizable interaction means that the effect of one factor is markedly dependent on the level of the other, and when quoting the effect of one factor, it is necessary to specify also the level of the other. When the factors are quantitative, a large interaction usually signifies that the levels of the factors are spaced too widely, and more experimental work at intermediate levels may be required. If a qualitative factor has been examined, the results must be considered separately for each level of the qualitative factor.

It should also be noted that, in a case where the interaction (AB) is significant but the main effect (say of A) is not, it cannot be concluded that A has no effect. The existence of a significant interaction means that both A and B affect the response, but not independently. The nonsignificance of A means, in this case, that A affects the response in different ways at the different levels of B, and that when its effect is averaged over the levels of B used in the experiment, the average effect is small. In stating the effect of A, it is therefore required to state also the level of B, and vice versa.

Thus, only when the interaction can be assumed negligible can it be inferred that the factors operate independently, and conclusions based on the significance or nonsignificance of the main effects be legitimately drawn.

B. ANALYSIS OF VARIANCE--CORROSION DATA

In the analysis of variance of each of the four factorial experiments, the error variance and mean squares of all main effects and two-factor interactions were computed. The calculation of the mean squares of all interactions of order higher than the second could have been accomplished without much difficulty on the machine, but most of them did not seem to be of interest; they are usually not significant, and the number of them was quite large. For example, in the 50-hour test, which is a 2^6 factorial, the number of mean squares of interactions of order higher than the second is: $\binom{6}{3} + \binom{6}{4} + \binom{6}{5} + \binom{6}{6} = 42$. However, when it was desirable to make plots of corrosion level versus one quantitative factor with a second quantitative factor as parameter, the three-factor interaction mean squares of

these two factors with each of the other factors were computed, since they were useful in determining how many different plots need be made.

The mean squares and error variances are given for each experiment in Tables 10 through 13. Each mean square was tested for significance at three levels: 10, 5 and 1%. If a mean square was not significant at the 10% level, a zero appears in front of it in the table. If the ratio of mean square to error variance was greater than the appropriate 10% F-value but less than the 5%, a one appears; if greater than the 5% but less than 1%, a two; and if greater than the 1%, a three. These numbers from 0 to 3 may be considered to indicate nonsignificance, possible significance, significance and high significance, in that order. However, at least a 2 was required for accepting the main effect or interaction as significant. In other words, the test at the 5% level was used as the criterion for significance.

The form of the tables is that of a triangular matrix. The main effect mean squares appear in the main diagonal, and the off-diagonal elements are the mean squares of the two-factor interactions. The three-factor interactions which were calculated appear below the first triangular matrix.

A second triangular matrix was used to present the two-way tables of results. The main diagonal gives the main effect means, and the off-diagonal elements, the two-factor means. The first matrix can be used to assess the significance, and the second to determine the direction and magnitude of the main effects and two-factor interactions.

A set of curves was plotted for each factorial experiment except the 2000-hour test. In this experiment, the only significant quantitative factor was the combined chloride-oxygen variable investigated at two levels, and the presentation of these results in the form of two-way tables was considered adequate.

For the 50-hour experiment, it was desirable to plot the observed values of corrosion level versus chloride concentration with oxygen concentration as the parameter. From Table 10 it was seen that the main effect, all two-factor interactions and computed three-factor interactions of the stress factor are not significant. On the other hand, the main effects of the three qualitative factors and at least one of the interactions between each of these and the factors to be plotted are significant. Thus, it was necessary to make 2^3 separate graphs, one for each of the possible combinations of the levels of the three significant qualitative factors. Also, the observed values to be plotted could be obtained by averaging over the two levels of stress as well as over the triplicate results for each treatment combination.

TABLE 10

ANPP Corrosion Program--50-Hour Test
Significance and Mean Squares

	Oxygen		Chloride		Phase		Stress		Heat Treatment		Metal	
Oxygen	2	9.9463	3	1.0063	3	1.5588	1	1.6921×10^{-1}	3	4.1255×10^{-1}	0	4.005×10^{-5}
Chloride			3	2.9751	3	5.9855	0	9.6292×10^{-2}	0	1.2504×10^{-1}	0	1.1707×10^{-2}
Phase					3	1.7581×10^{1}	0	1.4629×10^{-1}	2	2.3379×10^{-1}	3	2.1463
Stress							0	1.2508×10^{-1}	0	8.7545×10^{-2}	0	4.3869×10^{-5}
Heat treatment									3	5.3667	2	2.9296×10^{-1}
Metal											3	2.7831×10^{-1}

Error variance = 5.5781×10^{-2} Standard deviation = 2.3618×10^{-1} mg

Significance and Mean Squares
of 3-Factor Interactions with Oxygen and Chloride

	Phase		Stress		Heat Treatment		Metal	
	3	3.0757	0	3.7444×10^{-2}	3	4.1268×10^{-1}	3	3.9388

TABLE 10 (continued)
ANPP Corrosion Program
50-Hour Test
Two-Way Table of Results (mg)

	Oxygen 1	Oxygen 15	Chloride 10	Chloride 1000	Phase Vapor	Phase Liquid	Stress Level Stressed	Stress Level Unstressed	Heat Treatment Annealed	Heat Treatment Stress Relieved	Metal Nickel	Metal Monel
Oxygen { 1 ppm	0.62		0.57	0.67	0.84	0.41	0.63	0.62	0.50	0.74	1.00	0.24
{ 15 ppm		1.08	0.88	1.27	1.47	0.69	1.02	1.13	0.86	1.29	1.46	0.70
Chloride { 10 ppm			0.73		0.85	0.60	0.72	0.73	0.53	0.92	1.11	0.34
{ 1000 ppm				0.97	1.45	0.50	0.93	1.02	0.83	1.12	1.39	0.60
Phase { Vapor					1.15		1.10	1.21	1.02	1.29	1.64	0.67
{ Liquid						0.55	0.55	0.55	0.35	0.79	0.82	0.27
Stress { Stressed							0.82		0.68	0.97	1.21	0.44
{ Unstressed								0.88	0.69	1.09	1.26	0.50
Heat treatment { Annealed									0.68		1.02	0.34
{ Stress relieved										1.02	1.44	0.60
Metal { Nickel											1.23	
{ Monel												0.47

TABLE 11
ANPP Corrosion Program--200-Hr Test
Significance and Mean Squares

	Oxygen	pH Control	Phase	Stress	Heat Treatment	Metal	Chloride
Oxygen	3 5.387×10^1		3 2.5797	0 2.2729×10^{-1}	2 7.1870×10^{-1}	3 5.2956×10^1	3 2.0297×10^1
pH control		2 8.2858×10^{-1}	0 2.7751×10^{-1}	1 6.8375×10^{-1}	2 1.1779	0 1.6785×10^{-1}	3 5.7534
Phase		3 5.2619	3 2.0194×10^1	0 7.7057×10^{-3}	2 1.0979	3 2.8263	3 1.0467×10^1
Stress level				2 1.1608	0 2.6794×10^{-2}	0 4.4690×10^{-1}	0 2.1932×10^{-1}
Heat treatment					3 1.5998	3 1.3560	2 6.2292×10^{-1}
Metal						3 1.4557	3 5.4053
Chloride							3 4.3168×10^1

Error variance = 1.8497×10^{-1}

Standard error = 4.3008×10^{-1} mg

Significance and Mean Squares of 3-Factor Interaction with Oxygen and Chloride

pH Control	Phase	Stress Level	Heat Treatment	Metal
3 2.3026	2 5.6636×10^{-1}	0 1.2505×10^{-1}	1 4.2786×10^{-1}	3 3.6745×10^1

TABLE 11 (continued)
Two-Way Table of Results (mg.)

	Oxygen		pH Control		Phase		Stress		Heat Treatment		Metal		Chloride		
	1	15	NaOH	Na$_3$PO$_4$	Vapor	Liquid	Stressed	Unstressed	Annealed	Stress Relieved	Nickel	Monel	10	100	1000
Oxygen — 1 ppm	1.10		0.96	1.23	1.22	0.97	1.16	1.03	1.01	1.18	1.35	0.84	1.09	0.93	1.26
Oxygen — 15 ppm		1.71	1.65	1.76	1.96	1.45	1.73	1.68	1.69	1.72	1.35	2.06	1.33	1.17	2.62
pH Control — NaOH			1.31		1.47	1.14	1.32	1.30	1.21	1.40	1.25	1.36	1.31	0.89	1.72
pH Control — Na$_3$PO$_4$				1.50	1.71	1.29	1.58	1.42	1.49	1.50	1.45	1.55	1.11	1.21	2.16
Phase — Vapor					1.59		1.63	1.55	1.49	1.68	1.47	1.71	1.31	1.07	2.39
Phase — Liquid						1.21	1.26	1.17	1.20	1.22	1.23	1.19	1.12	1.03	1.49
Stress — Stressed							1.45		1.39	1.51	1.42	1.47	1.24	1.07	2.02
Stress — Unstressed								1.36	1.31	1.40	1.28	1.43	1.18	1.03	1.86
Heat treatment — Annealed									1.35		1.25	1.45	1.09	1.04	1.91
Heat treatment — Stress relieved										1.45	1.45	1.46	1.33	1.06	1.97
Metal — Nickel											1.35		1.28	1.08	1.70
Metal — Monel												1.45	1.15	1.02	2.18
Chloride — 10 ppm													1.21		
Chloride — 100 ppm														1.05	
Chloride — 1000 ppm															1.94

TABLE 12
ANPP Corrosion Program
2000-Hr Tests
Mean Squares and Significance

	Chloride-Oxygen	Stress	Phase	Heat Treatment	Metal
Chloride-Oxygen	3 4.9997×10^{1}	0 4.3891×10^{-1}	0 4.1175	0 5.8202	2 1.0568×10^{1}
Stress		0 2.0626×10^{-1}	0 2.5467	0 4.0167	0 3.1704
Phase			0 3.0497	0 4.8419×10^{-1}	0 4.1096
Heat treatment				0 3.8514	3 1.1857×10^{1}
Metal					3 7.5940×10^{2}

Error variance = 2.2981   Standard deviation = 1.516 mg

TABLE 12 (continued)
Two-Way Table of Results (mg)

	Chloride-Oxygen 10 ppm Cl 1 ppm O_2	Chloride-Oxygen 1000 ppm Cl 15 ppm O_2	Stress Stressed	Stress Unstressed	Phase Vapor	Phase Liquid	Heat Treatment Annealed	Heat Treatment Stress Relieved	Metal Nickel	Metal Monel	Metal Inconel
Chloride-Oxygen { 10 Cl, 1 O_2	5.44		5.54	5.35	5.42	5.47	5.48	5.41	6.71	9.05	0.57
Chloride-Oxygen { 1000 Cl, 15 O_2		4.27	4.25	4.28	4.58	3.95	3.90	4.63	4.79	7.57	0.44
Stress { Stressed			4.89		4.91	4.88	4.56	5.22	6.06	8.11	0.52
Stress { Unstressed				4.82	5.10	4.54	4.82	4.82	5.44	8.51	0.50
Phase { Vapor					5.00		4.78	5.22	5.93	8.73	0.34
Phase { Liquid						4.71	4.60	4.82	5.57	7.89	0.67
Heat treatment { Annealed							4.69		5.33	8.72	0.03
Heat treatment { Stress relieved								5.02	6.17	7.90	0.99
Metal { Nickel									5.75		
Metal { Monel										8.31	
Metal { Inconel											0.51

TABLE 13
ANPP Corrosion Program
Combined 50-, 200- and 2000-Hr Tests
Mean Squares and Significance

	Chloride-Oxygen	Stress	Phase	Heat Treatment	Metal	Time
Chloride-Oxygen	2 5.1215	0 2.6837×10^{-1}	3 2.5145×10^{1}	0 9.4475×10^{-1}	0 2.2220	3 7.7210×10^{1}
Stress		0 4.9310×10^{-1}	0 2.9600	0 2.2044	1 4.4995	0 5.5265×10^{-1}
Phase			3 4.3712×10^{1}	0 1.1120	2 7.9660	0 5.8715×10^{-1}
Heat treatment				0 6.4370×10^{-1}	2 5.8650	0 3.9200×10^{-1}
Metal					3 8.8890×10^{1}	3 5.5650×10^{1}
Time						3 1.0170×10^{3}

Error variance = 1.2473   Standard error = 1.1168 mg

Significance and Mean Squares of 3-Factor Interactions with Chloride-Oxygen and Time

Stress	Phase	Heat Treatment	Metal
0 7.4240×10^{-1}	0 5.1365×10^{-1}	3 6.7635	0 4.8532×10^{-1}

TABLE 13 (continued)
Two-Way Table of Results (mg)

	Chloride-Oxygen		Stress		Phase		Heat Treatment		Metal		Time		
	10 ppm Cl 1 ppm O₂	1000 ppm Cl 15 ppm O₂	Stressed	Unstressed	Vapor	Liquid	Annealed	Stress Relieved	Nickel	Monel	50	200	2000
Chloride-Oxygen { 10 Cl, 1 O₂	3.19		3.27	3.12	3.29	3.10	3.20	3.18	2.73	3.66	0.57	1.13	7.88
{ 1000 Cl, 15 O₂		3.46	3.47	3.45	4.15	2.77	3.36	3.56	2.82	4.10	1.27	2.93	6.18
Stress { Stressed			3.37		3.66	3.08	3.23	3.50	2.94	3.80	0.88	2.14	7.08
{ Unstressed				3.29	3.78	2.79	3.33	3.25	2.60	3.97	0.96	1.92	6.98
Phase { Vapor					3.72		3.61	3.83	2.99	4.44	1.35	2.47	7.33
{ Liquid						2.94	2.95	2.92	2.55	3.33	0.49	1.59	6.73
Heat treatment { Annealed							3.28		2.58	3.98	0.80	2.01	7.02
{ Stress relieved								3.37	2.96	3.79	1.04	2.04	7.04
Metal { Nickel									2.77		1.16	1.40	5.75
{ Monel										3.88	0.69	2.65	8.31
Time { 50											0.92		
{ 200												2.03	
{ 2000													7.03

Therefore, each plotted point is the mean of six observed values. These graphs are shown in Figs. 17 through 24.

Before a particular plot could be made, it was necessary to examine a two-way table between chloride and oxygen for the particular combination of levels of the three significant qualitative factors. An analysis of variance performed on such a table was used as a guide in drawing lines on the particular plot. For Figs. 17 through 20 and 24 the main effects of the oxygen and chloride and the interaction between them were significant when tested against the error variance, and, therefore, two lines were drawn.

For Fig. 21, the interaction was not significant, but both main effects were, and two lines were drawn. In Fig. 22, since none of the main effects and interaction was significant, a horizontal line was drawn at the mean of the four plotted points. The horizontal line is evidence that, in this case, chloride does not have an effect. That only one line is drawn indicates the main effect of oxygen to be nonsignificant and the interaction also to be negligible.

The analysis of variance for Fig. 23 showed the main effect of oxygen and the interaction to be significant, while the main effect of chloride was found to be negligible. From the graph, it can be seen that this is an example of the situation described in the previous section. Certainly, chloride has an effect, even though its main effect mean square is not significant. It simply has different effects at the different oxygen levels, i.e., the interaction is significant; and, when its effect is averaged over the levels of oxygen, the result is a small main effect.

For the 200-hour experiment, it was again desirable to plot corrosion level versus chloride with oxygen as the parameter. It can be seen from Table 12 that all computed interactions involving the stress factor are not significant. However, its main effect is significant at the 5% level. It was decided, therefore, to plot 16 curves (2^4), averaging over the levels of stress to obtain the points, but at the same time using, in the necessary significance tests, a new error variance which incorporated the main effect mean square of the stress factor. This new error variance, or pooled estimate, thereby eliminated the stress effect from consideration.

In the analyses of variance performed for each of the 16 curves, since three levels of chloride were investigated, the chloride main effect and the interaction with oxygen were partitioned into linear and quadratic components. Each of these four mean squares, as well as the oxygen main effect mean square, could then be individually
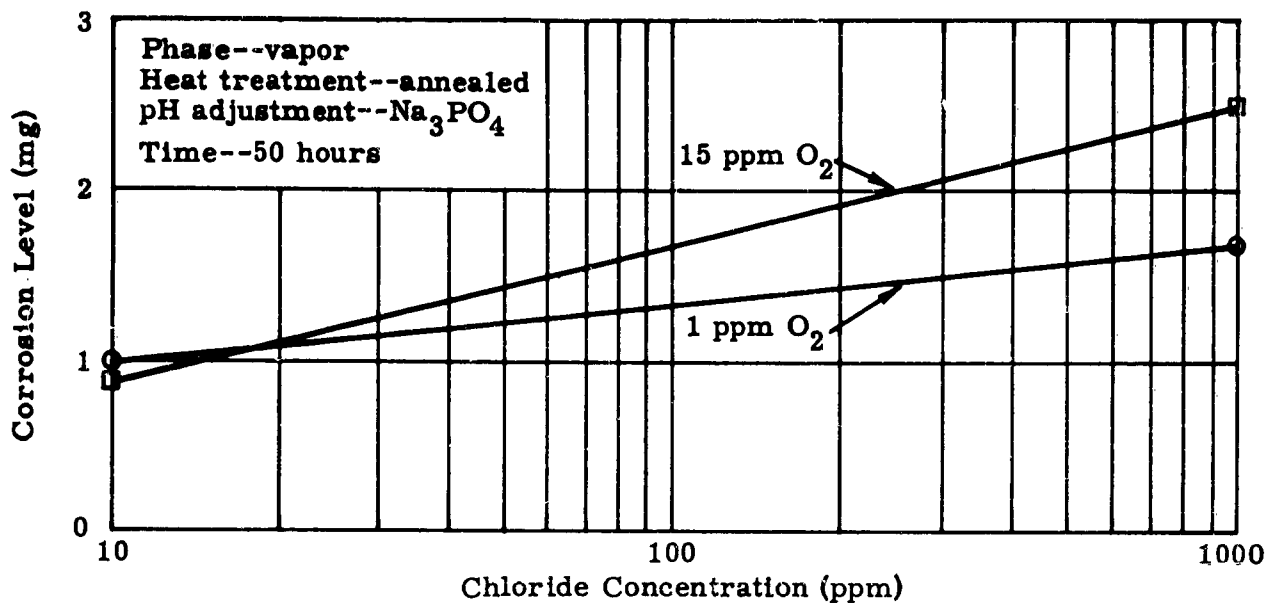
Fig. 17. Corrosion Level Versus Chloride Concentration for Nickel
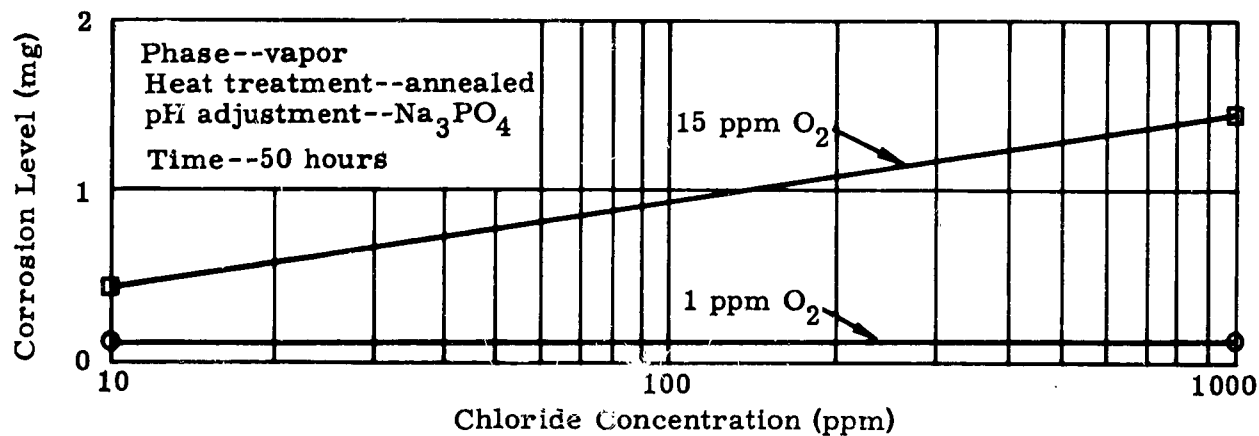
·Fig. 18. Corrosion Level Versus Chloride Concentration for Monel
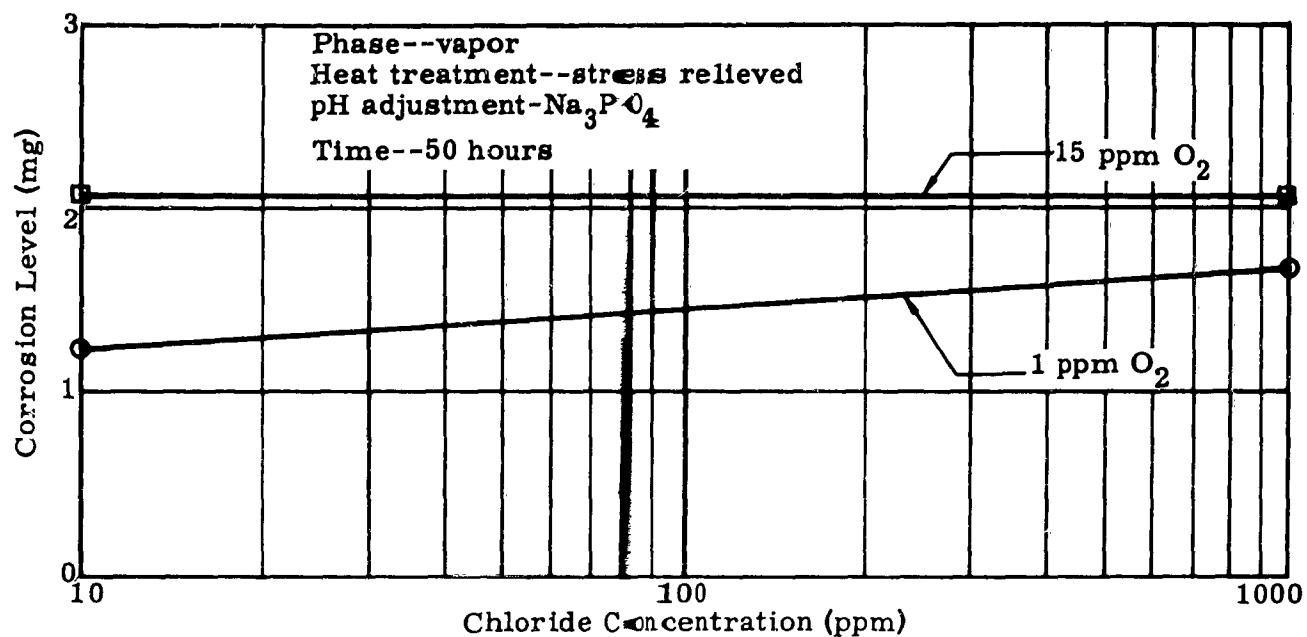
Fig. 19. Corrosion Level Versus Chloride Concentration for Nickel
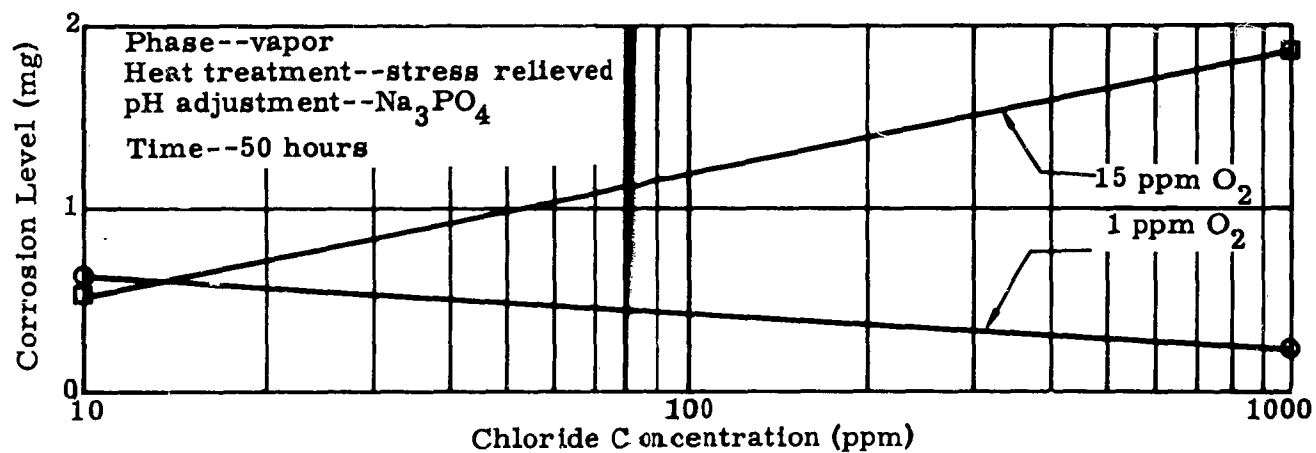
Fig. 20. Corrosion Level Versus Chloride Concentration for Monel
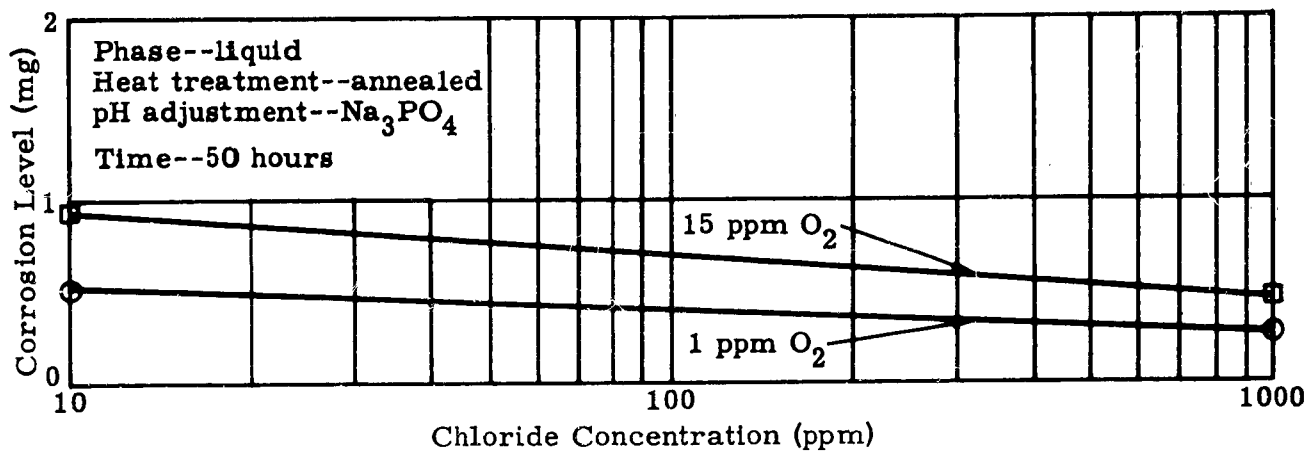
Fig. 21. Corrosion Level Versus Chloride Concentration for Nickel
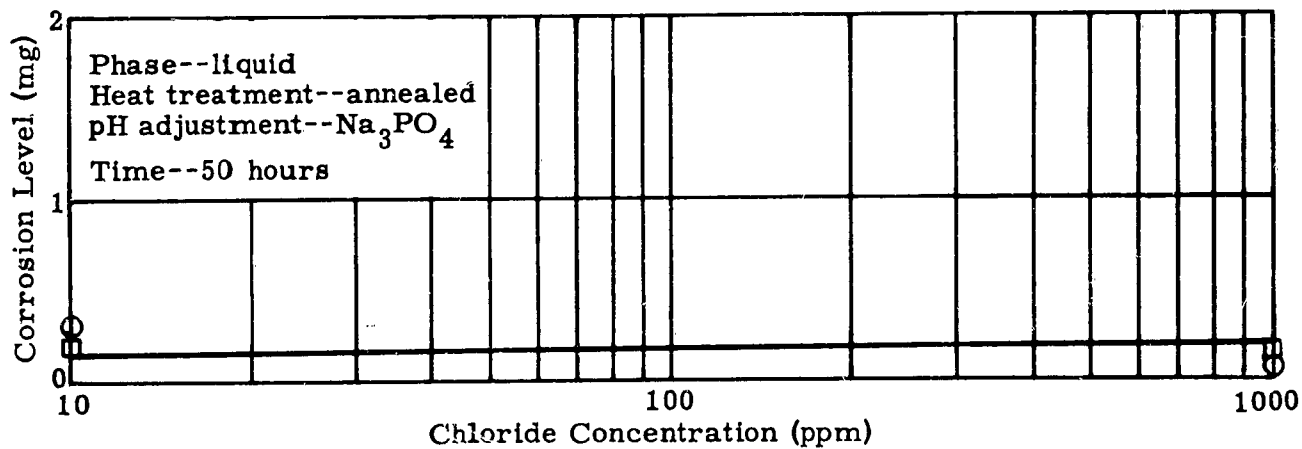
Fig. 22. Corrosion Level Versus Chloride Concentration for Monel
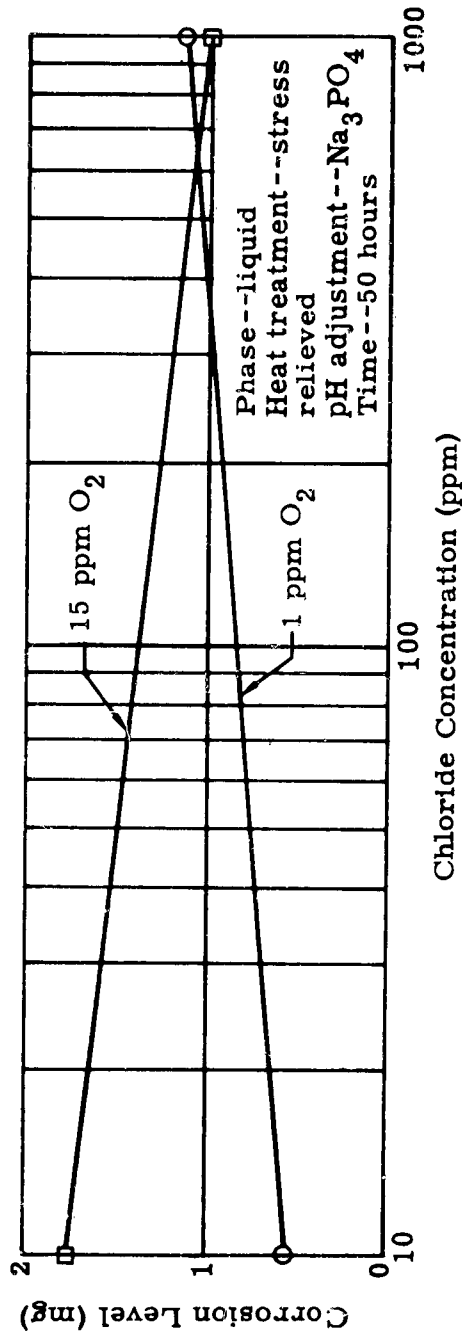
Fig. 23. Corrosion Level Versus Chloride Concentration for Nickel
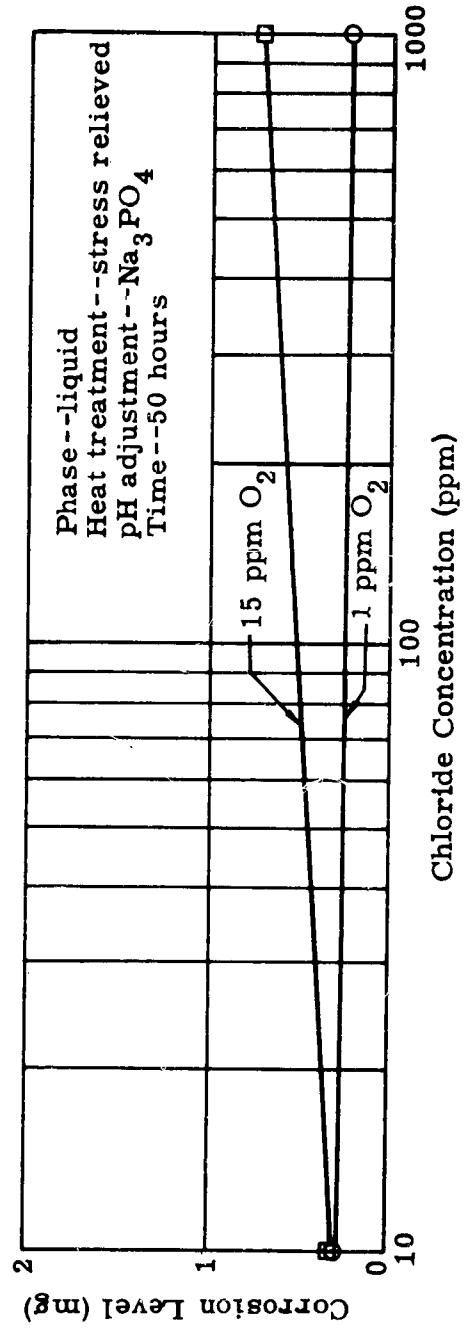
Fig. 24. Corrosion Level Versus Chloride Concentration for Monel

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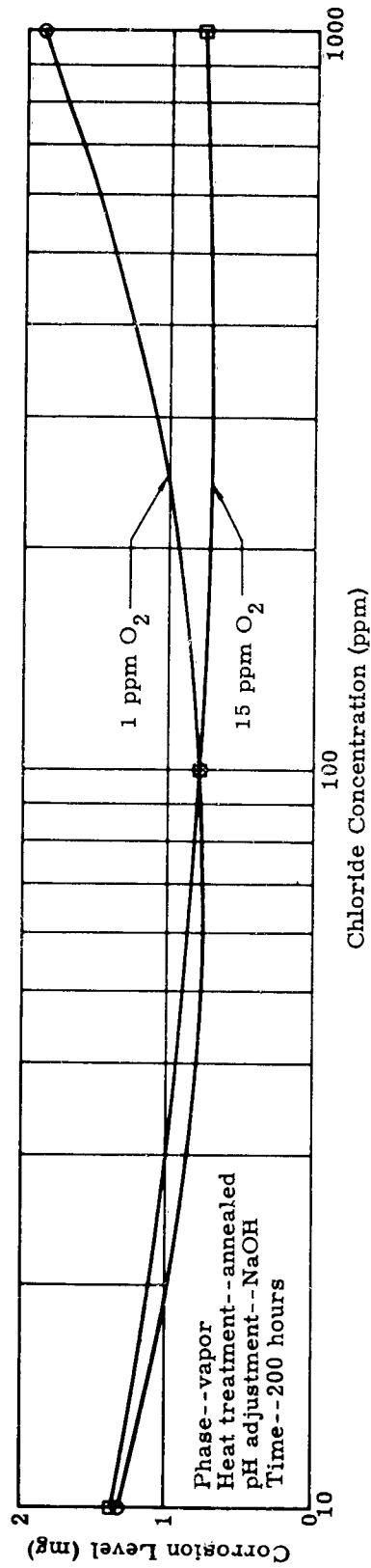
Fig. 25. Corrosion Level Versus Chloride Concentration for Nickel
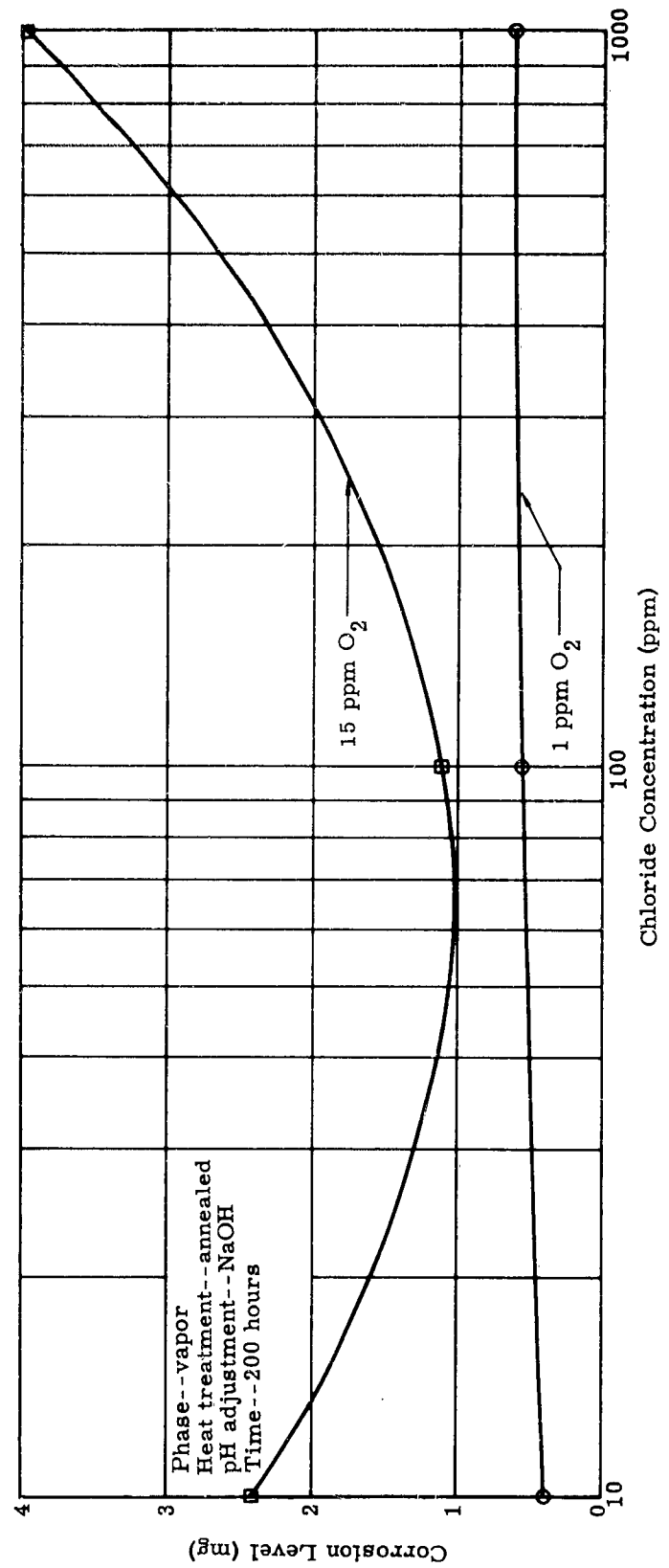
Fig. 26. Corrosion Level Versus Chloride Concentration for Monel

MND-E-2655
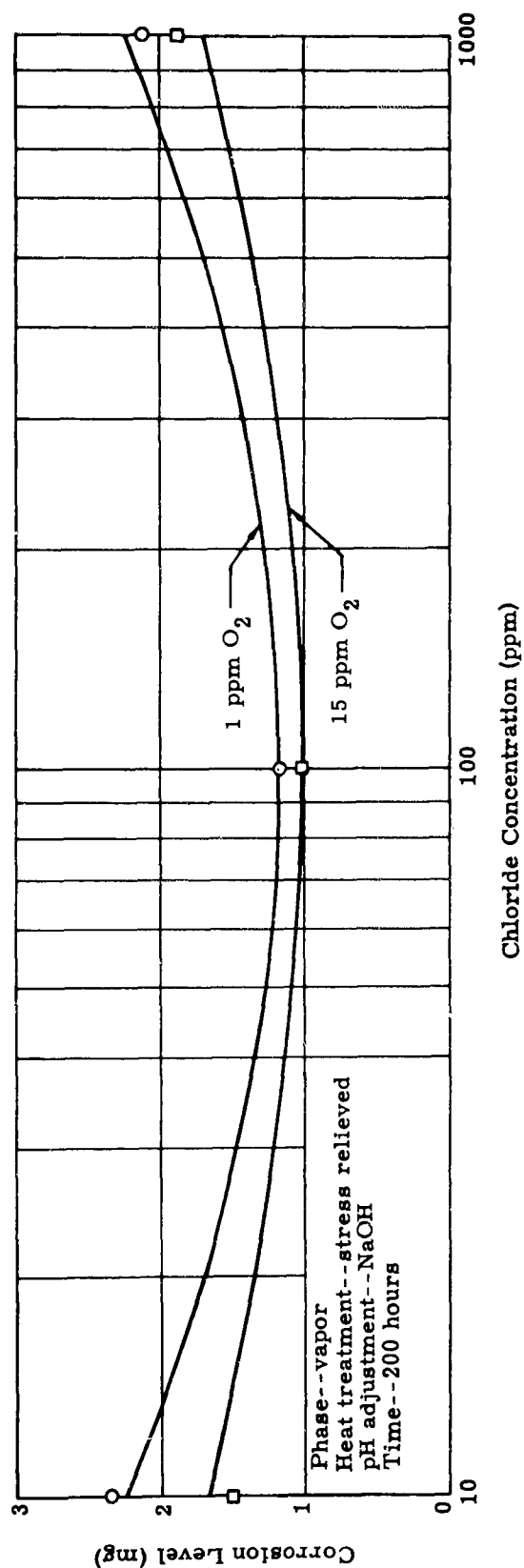
Fig. 27. Corrosion Level Versus Chloride Concentration for Nickel
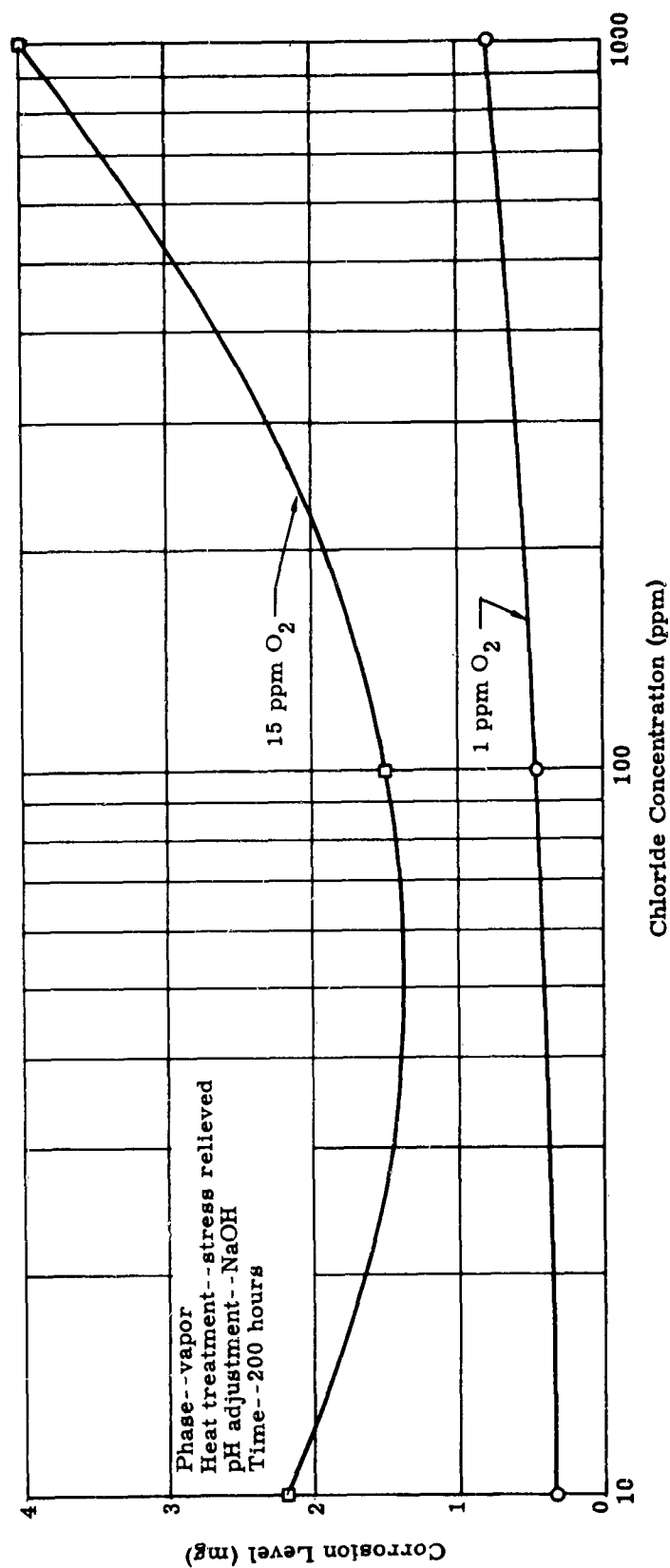
Fig. 28. Corrosion Level Versus Chloride Concentration for Monel
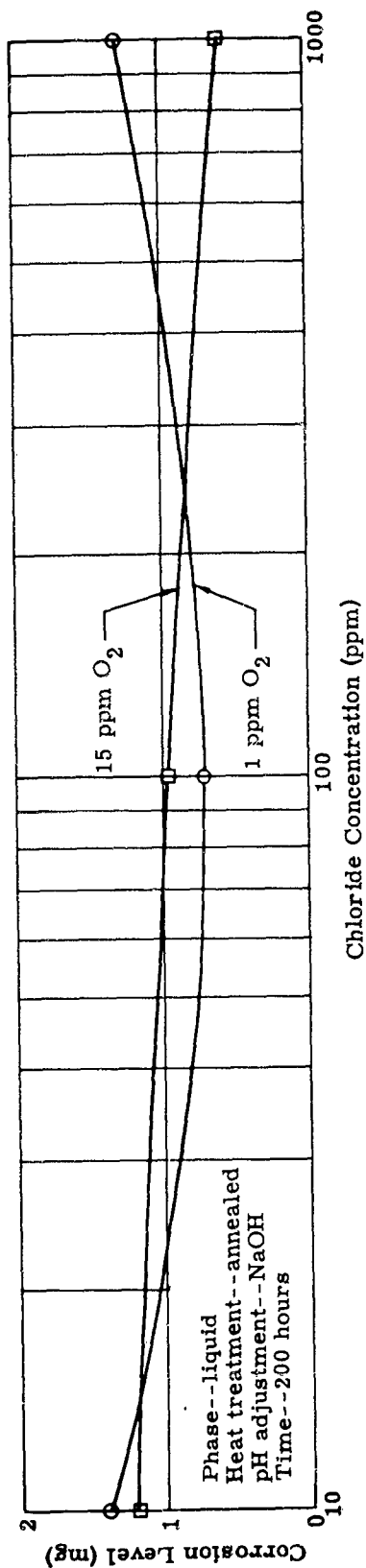
Fig. 29. Corrosion Level Versus Chloride Concentration for Nickel

Chloride Concentration (ppm)

Corrosion Level (mg)

15 ppm O_2

1 ppm O_2

Phase--liquid
Heat treatment--annealed
pH adjustment--NaOH
Time--200 hours

Fig. 30. Corrosion Level Versus Chloride Concentration for Monel

Chloride Concentration (ppm)

Corrosion Level (mg)

15 ppm O_2

1 ppm O_2

Phase--liquid
Heat treatment--annealed
pH adjustment--NaOH
Time--200 hours

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Phase--liquid
Heat treatment--stress relieved
pH adjustment--NaOH
Time--200 hours

1 ppm O₂

15 ppm O₂

Chloride Concentration (ppm)

Corrosion Level (mg)

Fig. 31. Corrosion Level Versus Chloride Concentration for Nickel

Phase--liquid
Heat treatment--stress relieved
pH adjustment--NaOH
Time--200 hours

15 ppm O₂

1 ppm O₂

Chloride Concentration (ppm)

Corrosion Level (mg)

Fig. 32. Corrosion Level Versus Chloride Concentration for Monel
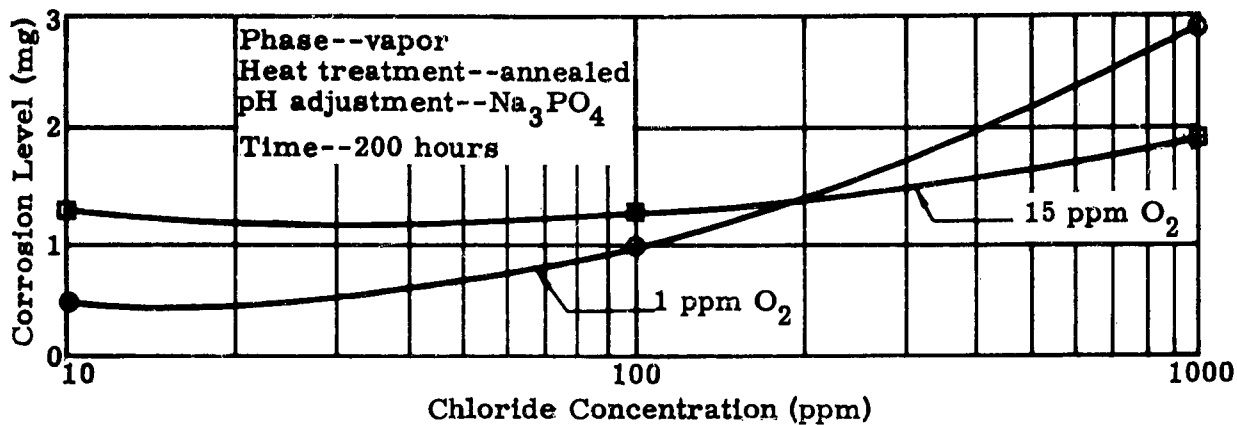
Fig. 33. Corrosion Level Versus Chloride Concentration for Nickel
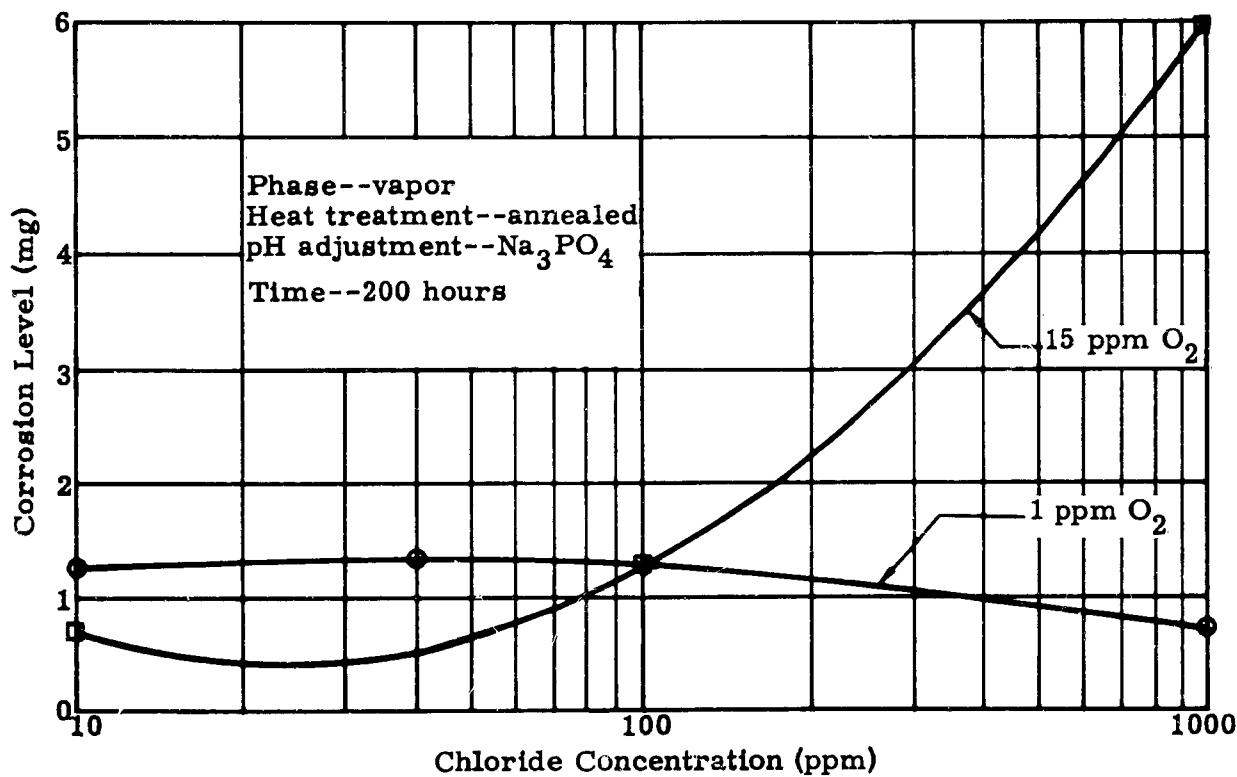
Fig. 34. Corrosion Level Versus Chloride Concentration for Monel
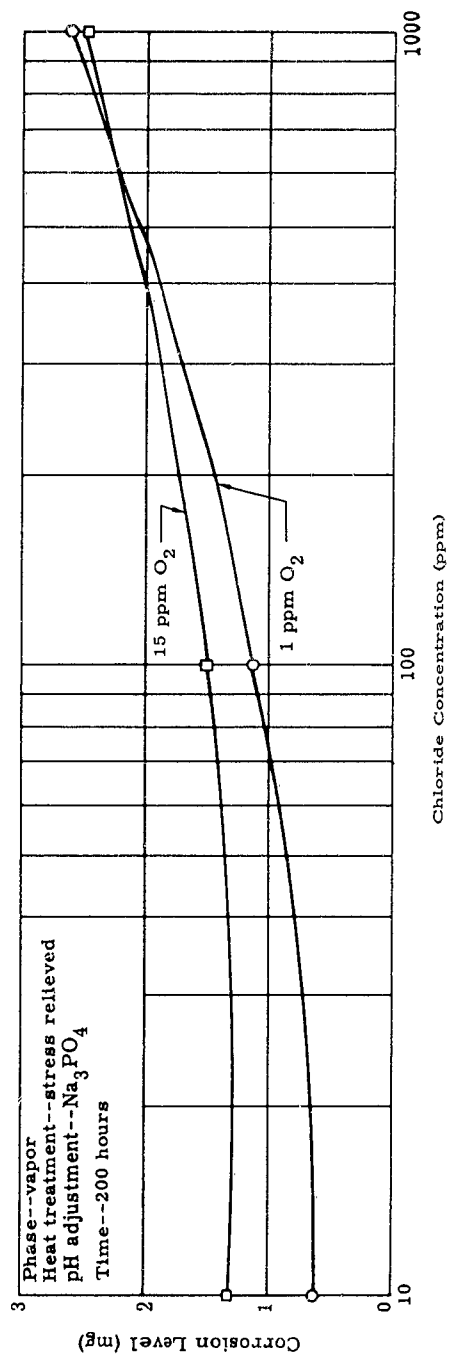
Fig. 35. Corrosion Level Versus Chloride Concentration for Nickel
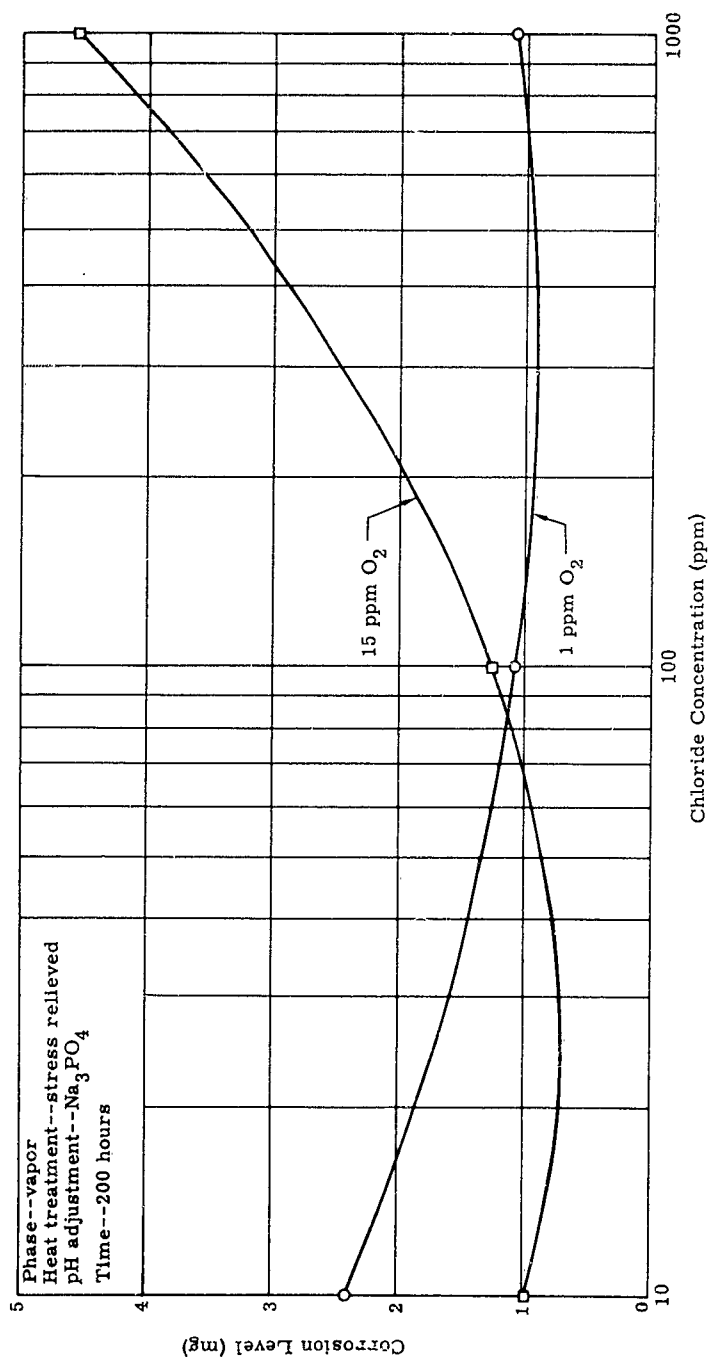
Fig. 36. Corrosion Level Versus Chloride Concentration for Monel

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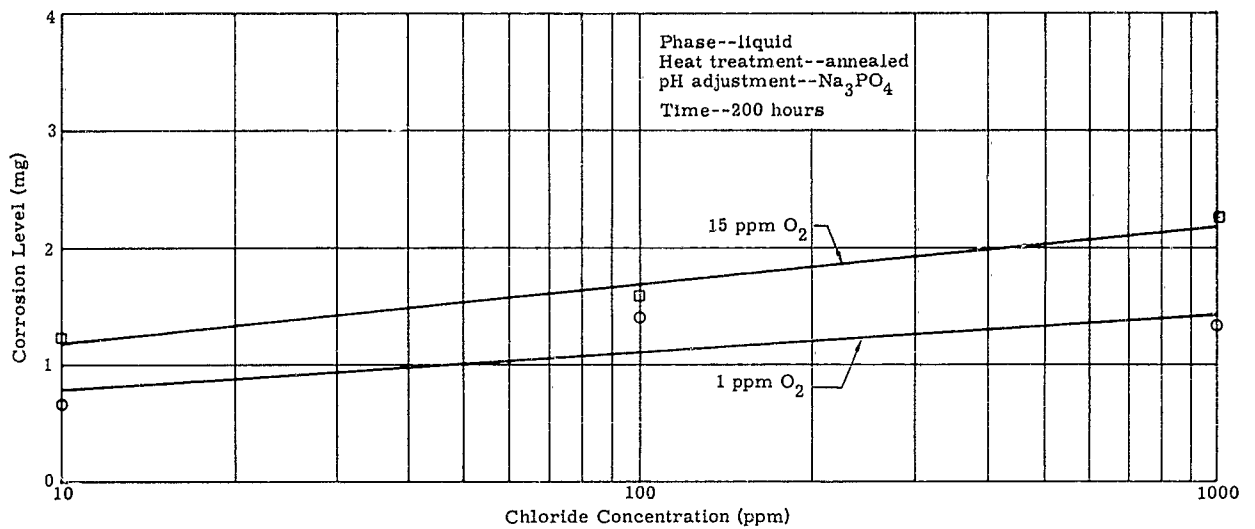
Fig. 37. Corrosion Level Versus Chloride Concentration for Nickel
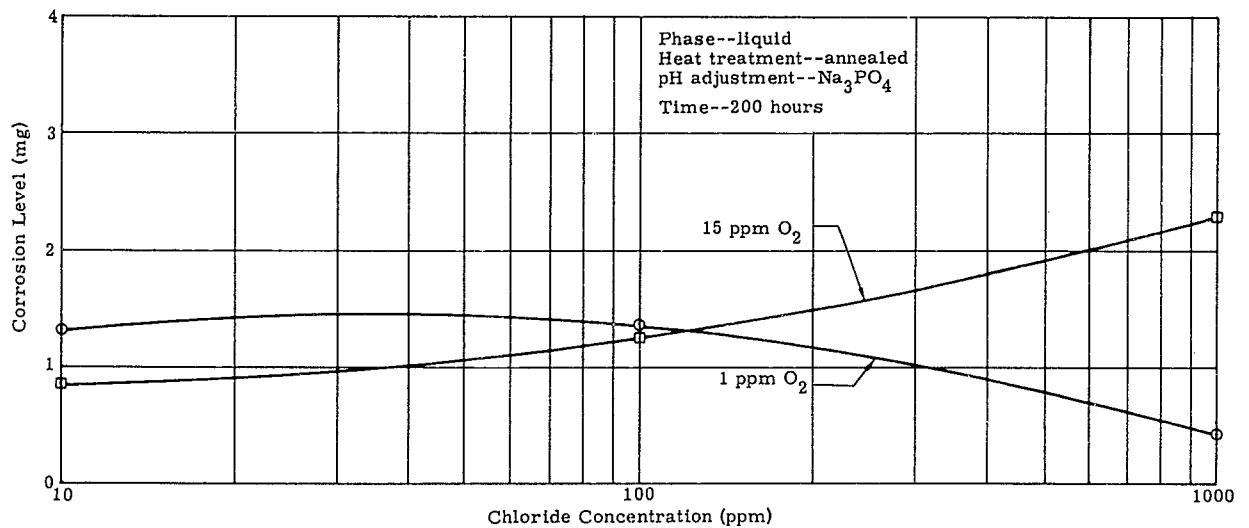
Fig. 38. Corrosion Level Versus Chloride Concentration for Monel
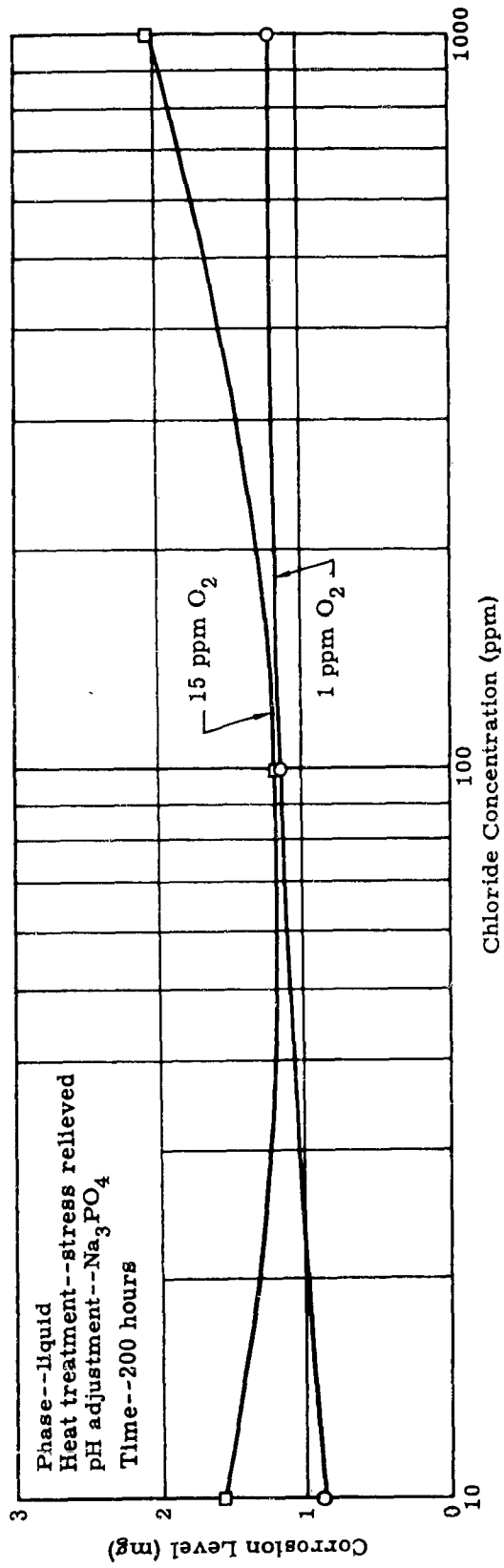
Fig. 39.   Corrosion Level Versus Chloride Concentration for Nickel
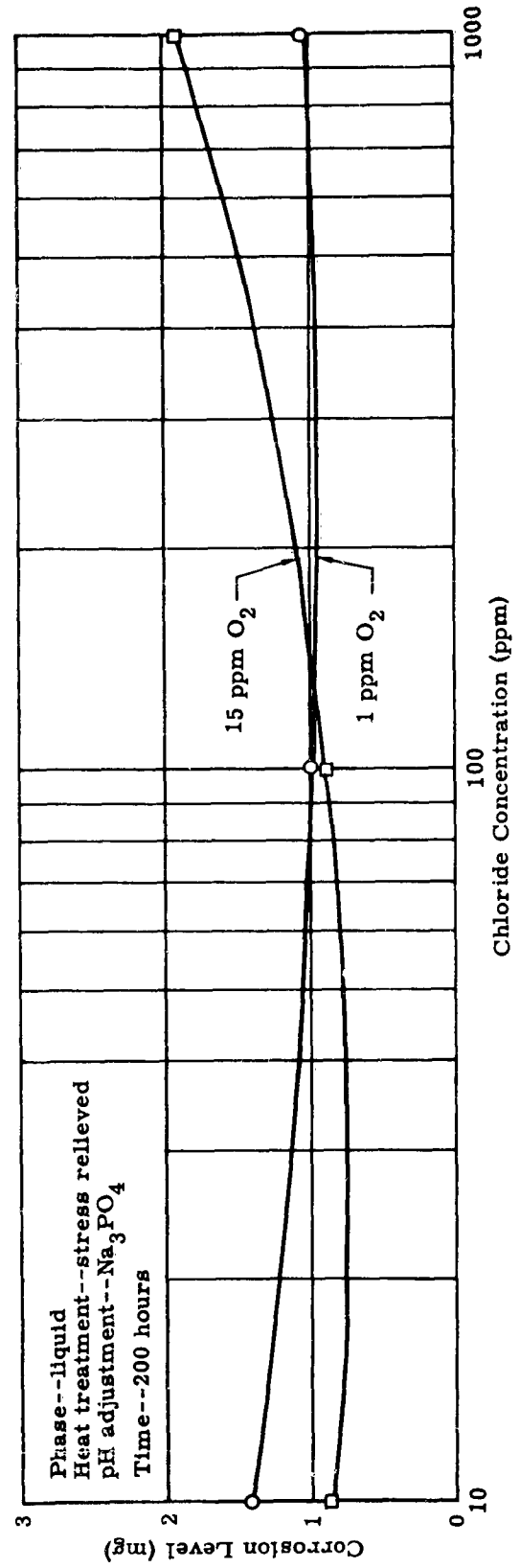
Fig. 40.   Corrosion Level Versus Chloride Concentration for Monel

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tested for significance, and the results used as a guide to whether straight lines or curves, and how many of each, should be drawn.

In cases where all five mean squares were significant, two curves were drawn. Each was the result of a least squares fit of the means at the three chloride levels, and the derived equation was of the form:

$$y = a + bx + cx^2.$$

Such an equation, of course, uniquely fits three points. Examples where this situation applies are Figs. 26, 28, 30, 34 and 36.

There were also cases where, for example, a linear main effect was not significant and the linear interaction was; or the oxygen main effect was not significant and one of the interaction components was; or neither interaction component was significant, but the oxygen main effect was; or both chloride main effects were not significant and both interactions components were. In these cases, two curves were plotted and the form of equation used to produce the least squares fits was that given above. Examples of these situations are Figs. 25, 29, 31, 33, 35, 38, 39 and 40.

For Fig. 27, both the linear chloride components and both inter-action components were not significant, while the oxygen main effect and the quadratic chloride component were. Therefore, least squares fits of the form

$$y = a + cx^2$$

were used, and two curves were drawn to show the oxygen effect.

For Fig. 37, the quadratic chloride component and both interaction components were not significant, while the oxygen main effect and the linear chloride component were. Thus, least squares fits of the form

$$y = a + bx$$

were made and two lines were drawn to show the effects of chloride and oxygen.

For the combined 50-, 200-, and 2000-hour experiment, it was desirable to plot corrosion level versus time with the chloride-oxygen variable as the parameter. As in the 50-hour experiment, it can be seen from Table 14 that the stress main effect and all computed interactions involving the stress factor were found to be non-significant. Thus, the corrosion weight losses could be averaged

over the levels of stress. At the same time, at least one of the computed interactions between the plotted quantitative factors and the three qualitative factors (phase, heat treatment and metal), was significant, and 2^3 graphs were required.

Since there are three levels of the time factor, linear and quadratic components were considered. For Figs. 41 through 46, both time main effect components were significant, as well as at least one of the interaction components or the chloride-oxygen main effect. Thus, two curves, uniquely fitting the points, were drawn.

For Figs. 47 and 48, both time main effect components were significant, but neither the chloride-oxygen main effect nor either of the interaction components was significant. Thus, at each of the three time levels, the results were averaged over the levels of chloride-oxygen, and one curve uniquely fitting these points was drawn.
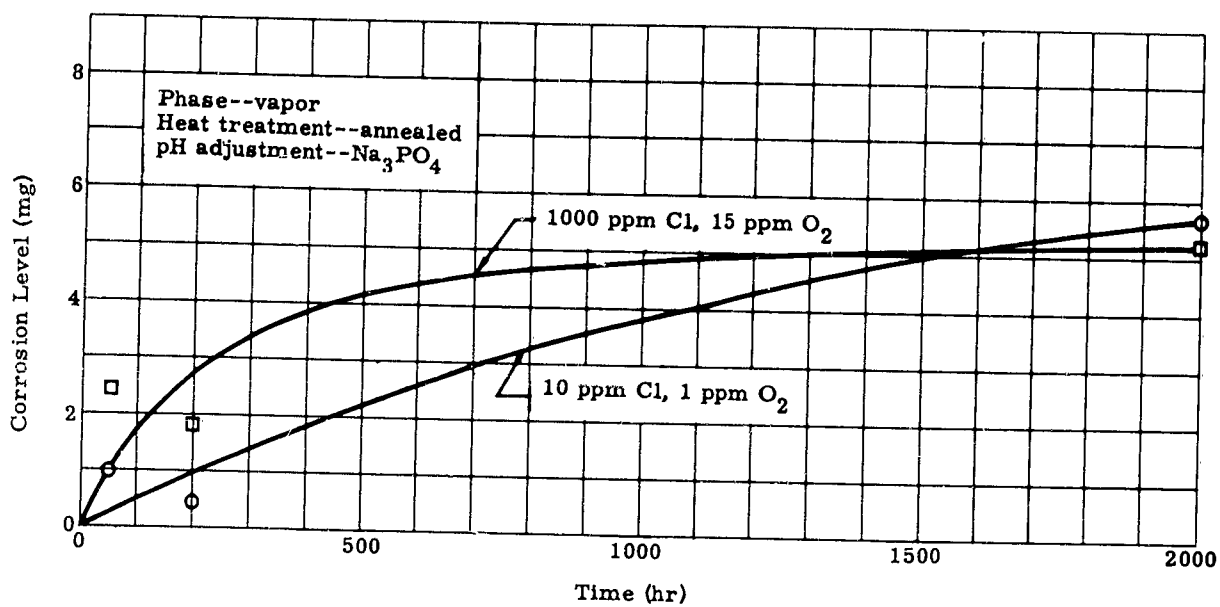
Fig. 41. Corrosion Level Versus Time for Nickel
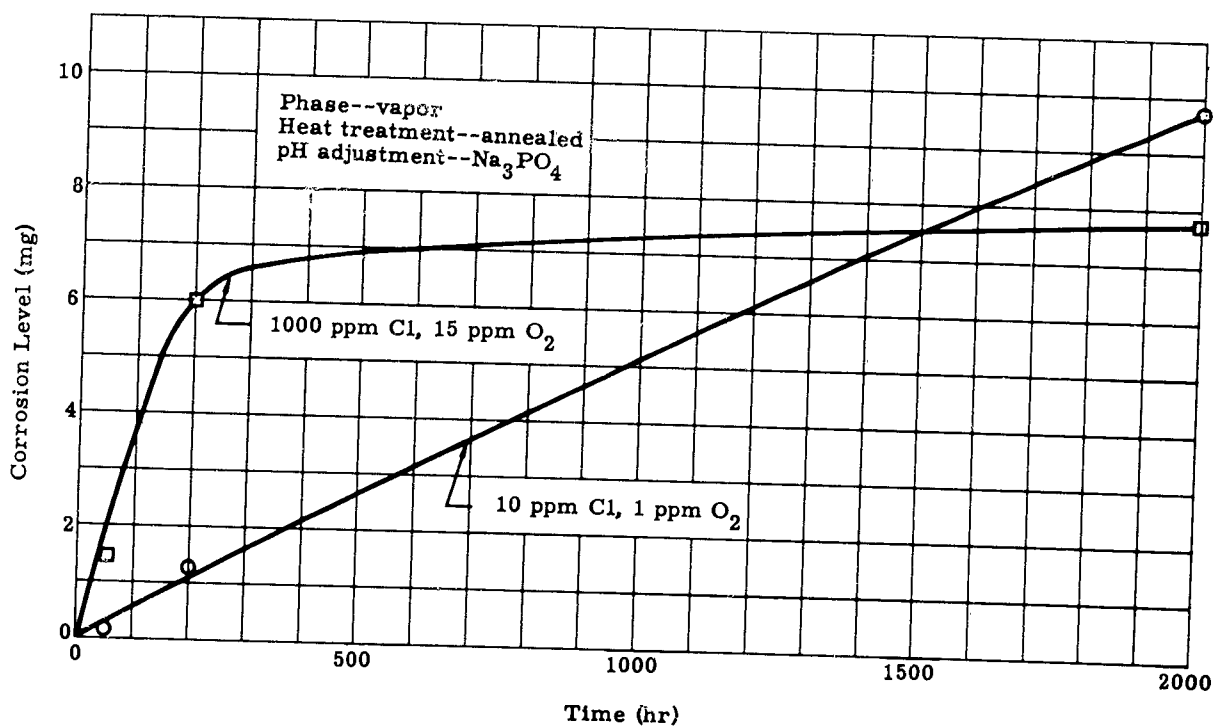
Fig. 42. Corrosion Level Versus Time for Monel
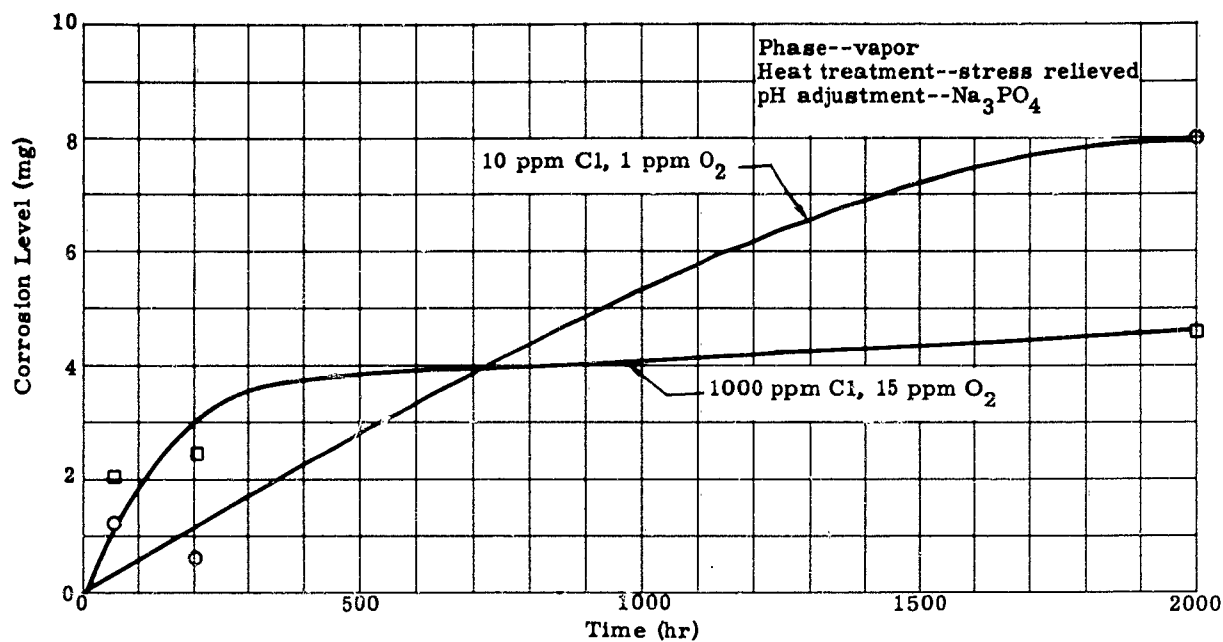
Fig. 43. Corrosion Level Versus Time for Nickel
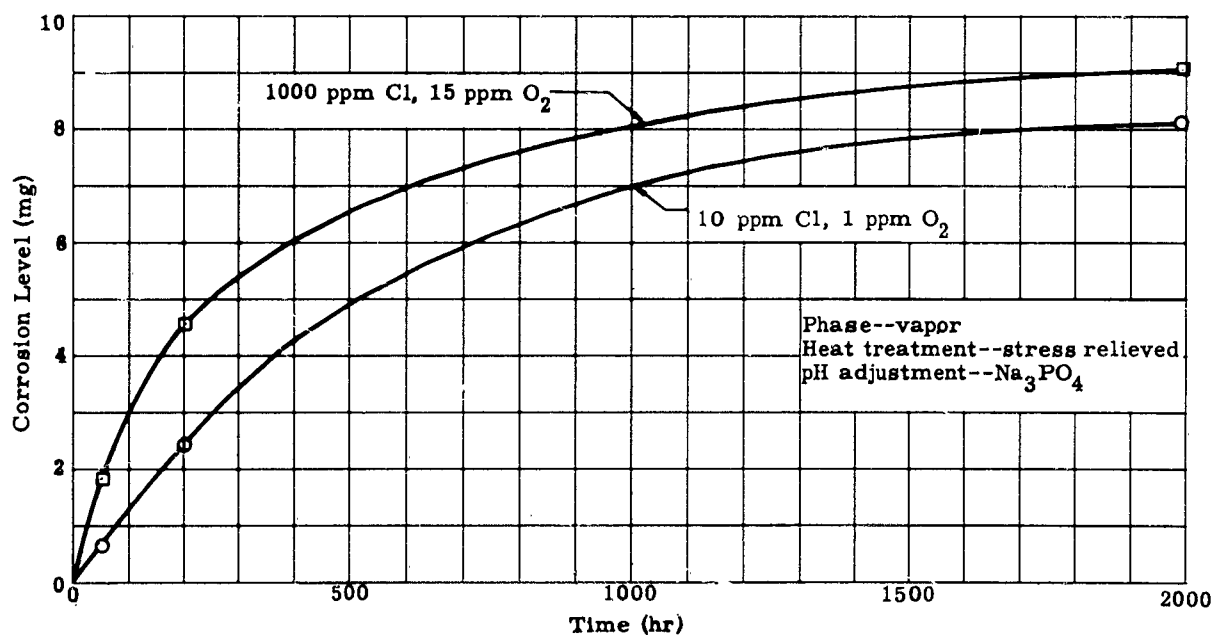
Fig. 44. Corrosion Level Versus Time for Monel

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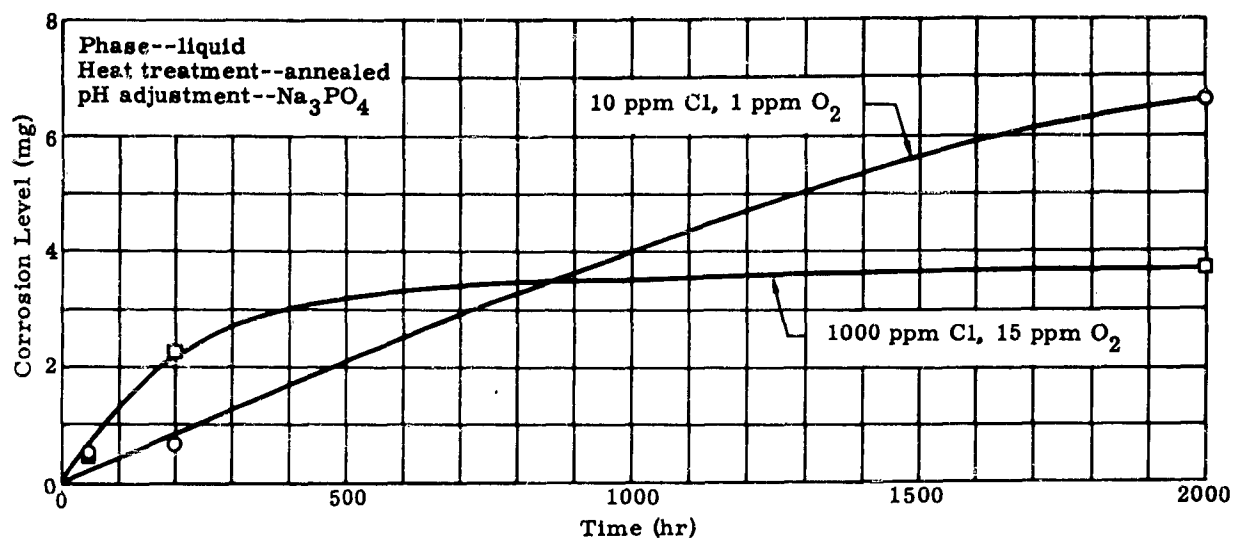
Fig. 45. Corrosion Level Versus Time for Nickel
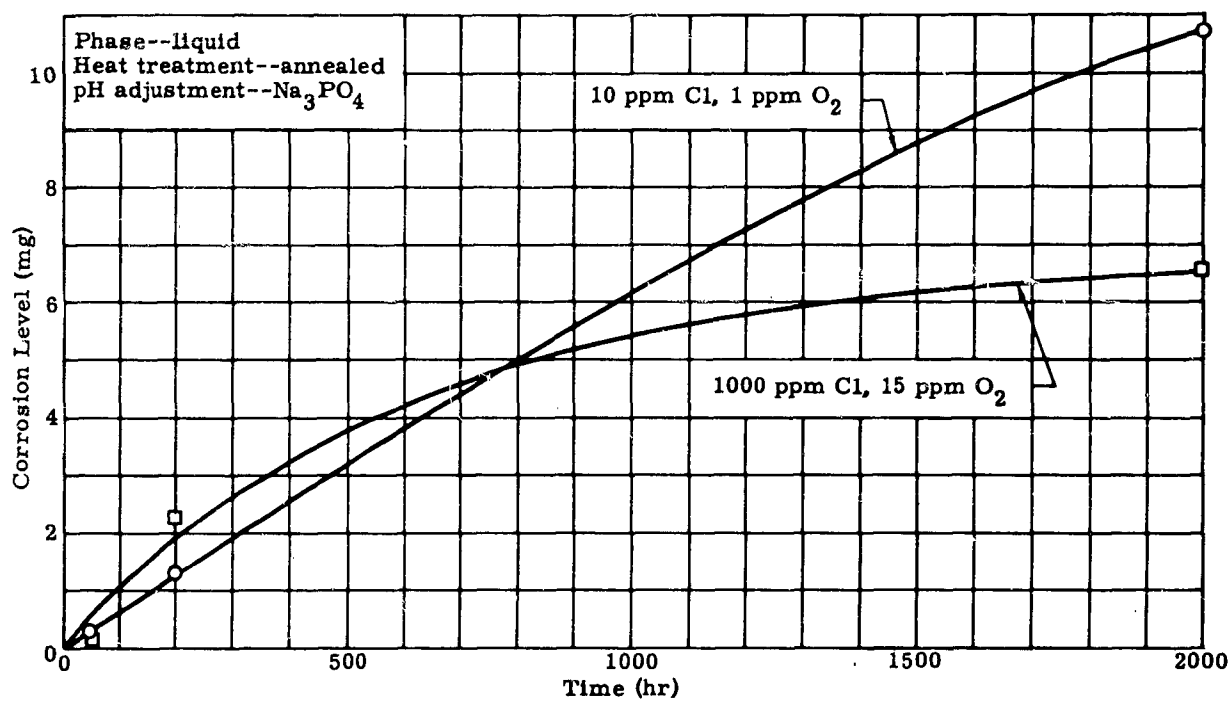
Fig. 46. Corrosion Level Versus Time for Monel

MND-E-2655
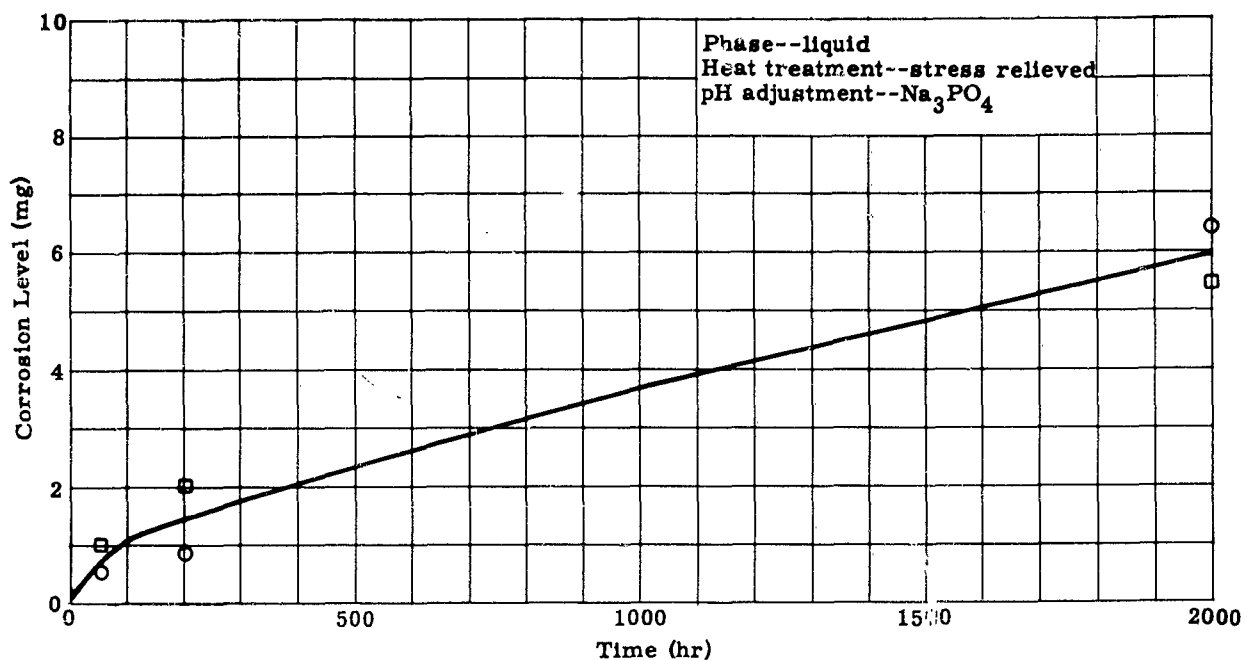
Fig. 47. Corrosion Level Versus Time for Nickel
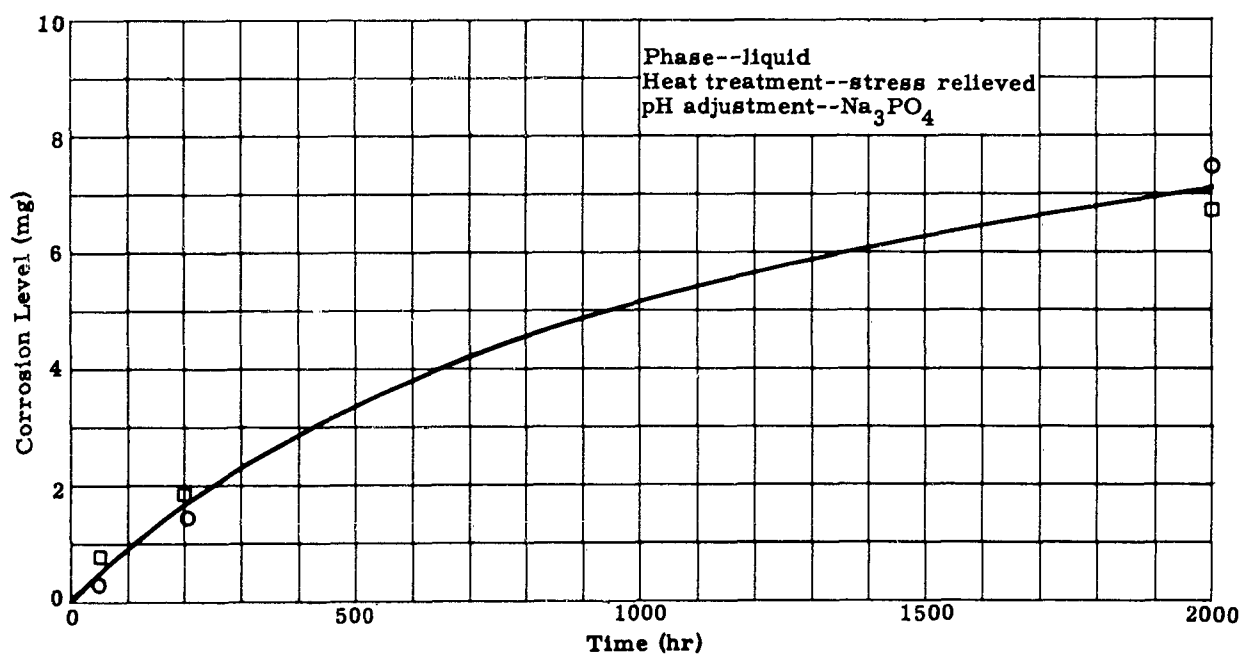
Fig. 48. Corrosion Level Versus Time for Monel

VII. CONCLUSIONS AND RECOMMENDATIONS

The results of these autoclave tests confirm that nickel, Monel and Inconel are not susceptible to stress corrosion cracking under the varied test conditions used, and their resistance to general corrosion is excellent, even for severe environmental exposure. The test results indicate that the corrosion rate of Inconel is much lower than Monel and nickel for comparable conditions. An incipient surface dulling was noted on some of the Monel and nickel specimens that were tested for 50 and 200 hours but none of the specimens cracked or pitted. No cracking of any coupons was observed in the 2000-hour autoclave tests, but varying degrees of attack and/or pitting did occur on all three materials (Monel, nickel and Inconel).

The conclusions resulting from the analysis of variance are presented below:

(1) The stress level was not a significant factor in the corrosion processes tested (all tests). However, it must be remembered that the stresses were primarily uniaxial and not nearly as complex as those stresses which occur in a fabricated component such as a steam generator.

(2) In general, the NaOH was a more favorable means of pH control than the Na_3PO_4. The major exception to this was at the lowest chloride level of 10 ppm (200-hour experiment). This is particularly interesting because nickel and nickel alloys are accepted as fully resistant to caustic; therefore, caustic treatment may be used with these materials.

(3) Inconel has the highest corrosion resistance of the metals tested (2000-hour experiment).

(4) In general, Monel is superior to nickel at 50 hours, while, after 200 and 2000 hours, nickel is more corrosion-resistant than Monel. The major exceptions occur in the 200-hour experiment, where the interactions with oxygen, phase, heat treatment and chloride are considerable (all tests).

(5) In general, corrosive attack on all metals is more severe in the vapor than in the liquid phase (all tests).

(6) The annealing heat treatment was generally slightly more advantageous than stress relieving; this is particularly evident in the 2000-hour Inconel tests. However, there are a number of exceptions to this conclusion (all tests). In actual practice, this is generally of academic interest because it is impossible to anneal a large complex structure.

(7) The lower oxygen concentration was more favorable. A few exceptions to this occurred in the 200-hour experiment (50- and 200-hour experiments).

(8) There was considerable interaction between the chloride and oxygen effects on corrosion. In many cases, an increase in chloride concentration (from lowest to highest) at lower oxygen decreased the amount of corrosion, while an increase in chloride concentration at higher oxygen increased the amount of corrosion. However, many exceptions to this statement occurred. In the 200-hour experiment there was much evidence of a minimum weight loss occurring between 10 and 100 ppm chloride concentrations for the higher oxygen concentration. This can be seen in Figs. 25 through 40 (50- and 200-hour experiments).

(9) The combined chloride-oxygen variable produced less corrosion when at its lower level (10 ppm chloride, 1 ppm oxygen) in the 50- and 200-hour exposure times, but after 2000 hours this influence was reversed and the higher level (1000 ppm chloride, 15 ppm oxygen) resulted in less corrosion (combined 50-, 200-, 2000-hour experiment).

(10) The rate at which corrosion occurred over the first 200 hours was for the most part considerably greater for the combined chloride-oxygen variable at its upper level. After 200 hours, the rate decreased and approached zero. For the combined variable at its lower level, the corrosion rate was essentially constant (combined 50-, 200-, 2000-hour experiment).

Corrosion rates in milligram per square decimeter per day for the three metals are listed in Table 14. These are time average rates from the results of the 2000-hour tests. The values are also averaged over the stressed, unstressed, annealed and stress relieved coupons. (The raw data is given in Table 7.) The significant superiority of Inconel is clearly evident.

TABLE 14

Comparison of Corrosion Rates for Inconel, Monel and Nickel

		Nickel (mdd)	Monel (mdd)	Inconel (mdd)
10 ppm chloride	Vapor	0.38	0.50	0.02
1 ppm oxygen	Liquid	0.36	0.51	0.04
1000 ppm chloride	Vapor	0.28	0.46	0.02
15 ppm oxygen	Liquid	0.26	0.37	0.03

It is indicated by the data shown in Table 14 and that presented graphically in Figs. 42, 43, 45 and 46 that in those systems where chloride is present in amounts within the range of these tests, it is advantageous to have considerably more than 1 ppm oxygen, presumably to maintain the protective oxide film. No attempt was made to determine if there is an optimum oxygen concentration. It cannot be supposed that 15 ppm oxygen necessarily approaches the optimum concentration required to maintain the natural protective oxide film. A similar protective mechanism has been suggested for other systems (Ref. 18) where other materials were involved.

On the basis of general overall applicability to high temperature water service, the three metals, as a result of this program, can be listed in their order of preference--Inconel, nickel and Monel. Specific qualities such as fabricability, thermal conduction, thermal expansion, strength, etc., may dictate a revision of this rating for some particular uses

However, the corrosion resistance of all three materials is sufficiently good to warrant further study. A limited amount of dynamic loop testing of these materials has been performed under the ANPP Corrosion Program. Additional loop tests should be considered as a means of obtaining more definitive information under conditions similar to actual service.

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The Martin Company
Nuclear Division, Baltimore, Maryland
AUTOCLAVE TESTING OF MONEL, NICKEL AND INCONEL

MND-E-2655   UNCLASSIFIED
J. McGrew, S. Frank, T. Page
October 1961   Pages
Contract DA-44-009-ENG-3581

Stressed and unstressed specimens of Monel, nickel and Inconel were exposed to varied environmental conditions to test the resistance of these three metals to corrosion. The experiments were conducted in autoclaves operated at 450° F and 422 psia for 50, 200 and 2000 hours. The environmental conditions included variations in concentration of chloride, oxygen, phase (liquid or vapor) and method of pH adjustment. Statistical methods were employed in designing the experiments and in analyzing the results.

An incipient surface dulling was noted on some of the specimens that were tested for 50 and 200 hours, but none of the specimens cracked or pitted. No cracking of any coupons was observed in the 2000-hour autoclave tests, but varying degrees of pitting did occur for all three metals.

Typical corrosion rates from the 2000-hour data for coupons exposed to 1000 ppm chloride and 15 ppm oxygen were: Monel, 0.50 mdd; nickel, 0.38 mdd; and Inconel, 0.02 mdd.

Based on the results of these tests, the materials are listed in order of preference as follows: Inconel, nickel and Monel.